The Synthesis of 1*H*- and 5*H*-Thieno[1,2]diazepines by the Electrocyclisation of α-(2-Alkenylthienyl)diazoalkanes, and Some Observations on their Photochemical Reactivity and Ring Inversion

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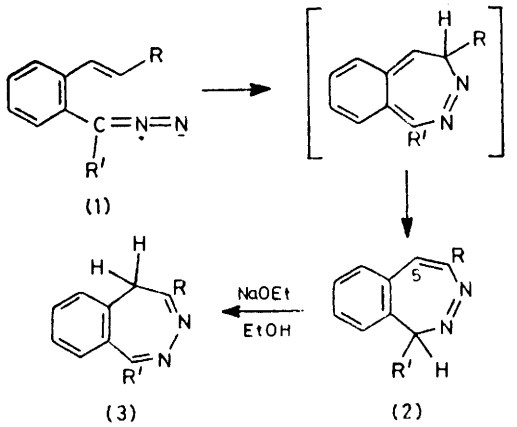
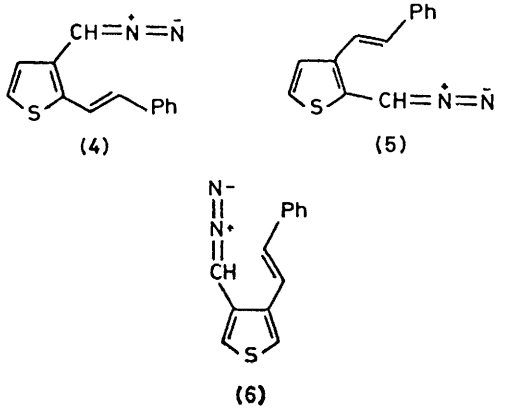
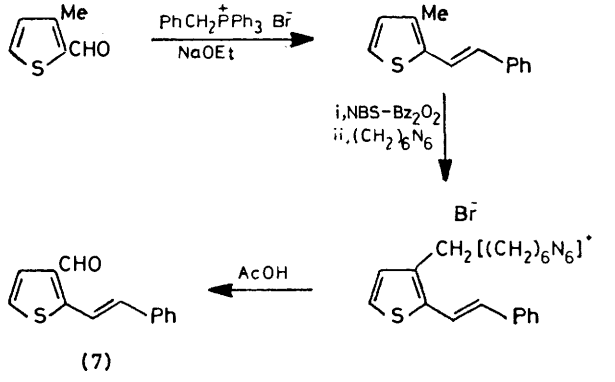
The cyclisation of the α-(2-alkenylthienyl)diazoalkanes (4) and (5) provides the first route to thieno[3,2-*d*]- and thieno[2,3-*d*]-[1,2]diazepines, (10) and (11) respectively. In contrast, 3-diazomethyl-4-(*trans*-2-phenylethenyl)thiophen (6) did not cyclise but gave carbene-derived products. The thieno[3*H*-1,2]diazepines (10) and (11) were converted by base into the isomeric thieno[4*H*-1,2]-diazepines (15) and (16) respectively and by u.v. irradiation into the diazeto[1,4-*a*]thieno[*c*]pyrroles (21) and (22). Variable-temperature proton n.m.r. studies have shown that the energy barrier to ring inversion is lower for the thienodiazepines than for analogous benzodiazepines.

THE 1,7-electrocyclic ring closure of α-(*o*-alkenylaryl)-diazoalkanes (1) provides the only route to 1*H*-2,3-benzodiazepines (2),[1] and the base-catalysed isomerisation of the latter is the most versatile and convenient route to the 5*H*-isomers (3).[2] The work described here is part of a programme undertaken to discover whether this principle could be used to synthesise new heterocyclic systems in which the 1,2-diazepine ring is fused to five-membered heteroaromatic rings. Thus we have examined the reactions of the diazo-compounds (4)—(6); these were derived from *p*-tolylsulphonylhydrazone precursors prepared from the aldehydes (7)—(9) which were synthesised by the routes shown in Schemes 1—3.



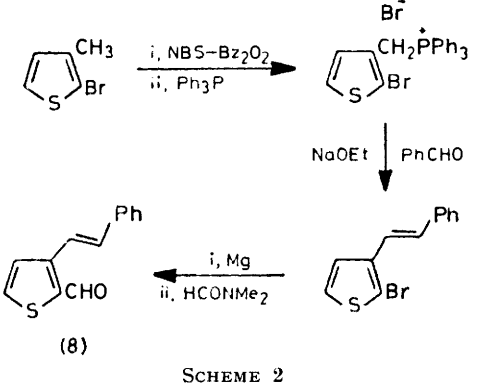


The reactions of the diazo-compounds (4) and (5) exactly paralleled those of the aryl analogues (1) and gave the thieno[3,2-*d*][1,2]diazepine (10) and the thieno-[2,3-*d*][1,2]diazepine (11) respectively in high yield.



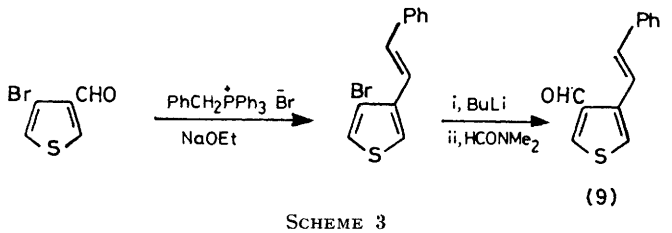
SCHEME 1

These products had very similar spectra to the 1*H*-2,3-benzodiazepines (2);[1] some comparative n.m.r. data are shown in structures (12)—(14). The thieno[3*H*-1,2]-diazepines (10) and (11) were readily isomerised to the thieno[4*H*-1,2]diazepines (15) and (16) respectively by sodium ethoxide in ethanol. These compounds also had similar spectra to the benzo-analogue (17).



SCHEME 2

As expected both classes of thienodiazepines showed ring inversion; the n.m.r. coalescence temperature and $\Delta G^{\ddagger}$ values calculated in the usual way [1] are given in



SCHEME 3

Table 1, together with those of the similarly substituted 2,3-benzodiazepines (12) and (17) for comparison. The values for the first set, the 3*H*-1,2-diazepines, are less

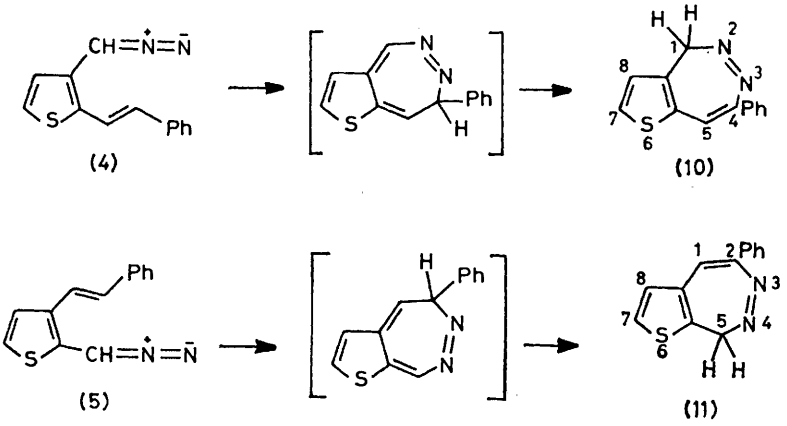
TABLE 1

Coalescence temperatures and free energies of activation for ring inversion of thieno- and benzo-[1,2]diazepines

Compound	T_c/°C *	$\Delta G^{\ddagger}$/kJ mol^{-1}
(12)	102 ± 10	72 ± 2
(10)	74 ± 10	66 ± 2
(11)	82 ± 10	68 ± 2
(17)	55 ± 2	65.6 ± 0.4
(15)	−1 ± 2	53.4 ± 0.4
(16)	−7 ± 2	51.8 ± 0.4

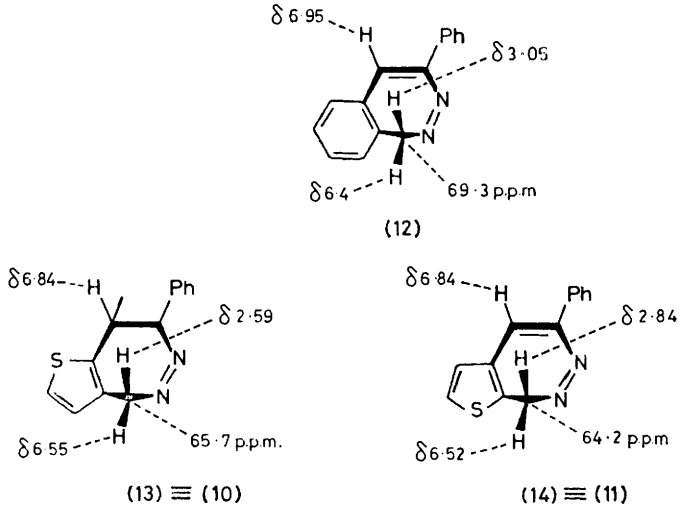
* Temperature of coalescence for the methylene protons.

ferences in (i) between the benzo- and thieno-diazepines are in accord with the observed trend. Considering



precise because of the greater difficulty in determining T_c when the chemical-shift difference is high.

It can be seen that for both diazepine classes the $\Delta G^{\ddagger}$

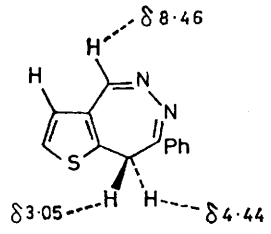


values are lower for the thieno- than the benzo-diazepines, the difference being greater for the 4*H*-1,2-diazepines (15)—(17) (*ca.* 12—14 kJ mol^{-1}) than for the 3*H*-isomers (10)—(12) (*ca.* 4—6 kJ mol^{-1}). There are several factors which affect the inversion barrier in these systems, *e.g.* (i) changes in both angle strain and in non-bonded interactions as the preferred ' bent ' conformer becomes planar in the transition state, and (ii) conjugative stabilisation of the planar transition state. The difference in (i) between the benzo- and thieno-diazepines are in accord with the observed trend. Considering first the changes in angle strain: a Dreiding model shows that the non-annelated diazepine ring (19) can pucker so that in its ' bent ' form all the angles have approximately their preferred values so that the angle θ between the external bonds on the *d* side is close to 60° as shown in the projection (19a). Thus the fusion of a benzene ring (18a) will contribute no extra angle strain but the fusion of a thiophen ring (18b) will have some destabilising effect. When the diazepine ring is flattened in the transition state for inversion (19b) the ring angles increase (to 128° for a symmetrical ring) and θ is compressed to *ca.* 51°; this will be resisted by the fused benzene ring but more readily accommodated by the fused thiophen ring. Thus in terms of angle strain the effect of substituting the thieno- for the benzo-ring is to destabilise the ' bent ' form and stabilise the planar transition state for inversion. A similar effect is predictable for non-bonded interactions: it was suggested [1] for the 5*H*-benzodiazepines (20) that the interaction between substituent X and the *peri*-hydrogen is

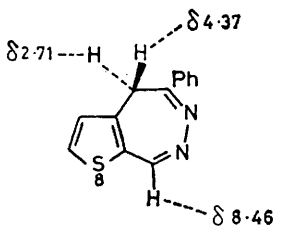
TABLE 2

Mass spectra of thieno[1,2]diazepines

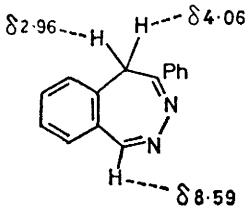
Compound	*m/e* (% Relative abundance)
(10)	226 (4), 198 (100), 19 (80), 171 (12), 165 (32), 153 (8), 152 (12), 139 (5), 121 (7), 98 (8)
(11)	226 (3), 198 (100), 197 (77), 171 (16), 165 (36), 153 (9), 152 (13), 139 (9), 121 (9), 98 (9)
(15)	226 (90), 123 (60), 103 (17), 96 (100), 28 (50)
(16)	226 (100), 123 (50), 103 (10), 96 (80), 28 (42)



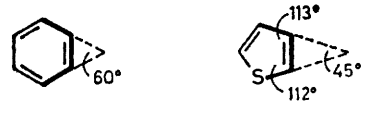
(15)



(16)



(17)



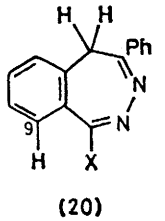
(a) (b)

(18)

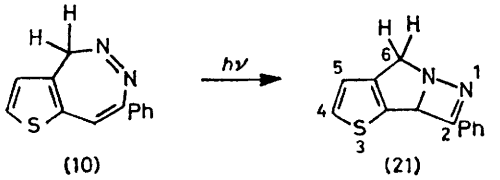
(a) (b)

(19)

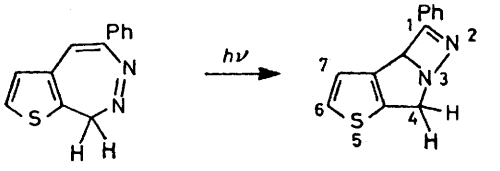
important since when X = H, Me, and *p*-tolyl $\Delta G^{\ddagger}$ values are 65.6, 83.2, and 92.4 kJ mol^{-1} respectively. A Dreiding model shows that even when X = H this interaction may still make some contribution to $\Delta G^{\ddagger}$ since the hydrogens approach to 2.1 Å in the planar state, which is within the sum of their van der Waals radii (2.4 Å). In the analogous thienodiazepines this interaction will be less important, *e.g.* in (16) due to the absence of a hydrogen at the 8-position and in (15) due to the reduced size of the fused ring and hence the greater separation of the hydrogens. A similar argument would be expected to apply to the 3*H*-1,2-diazepines (12), (10), and (11) but the sensitivity of this system to the effect is not known since no 1*H*-2,3-benzodiazepines (2) with substituents at the 5-position have been synthesised.



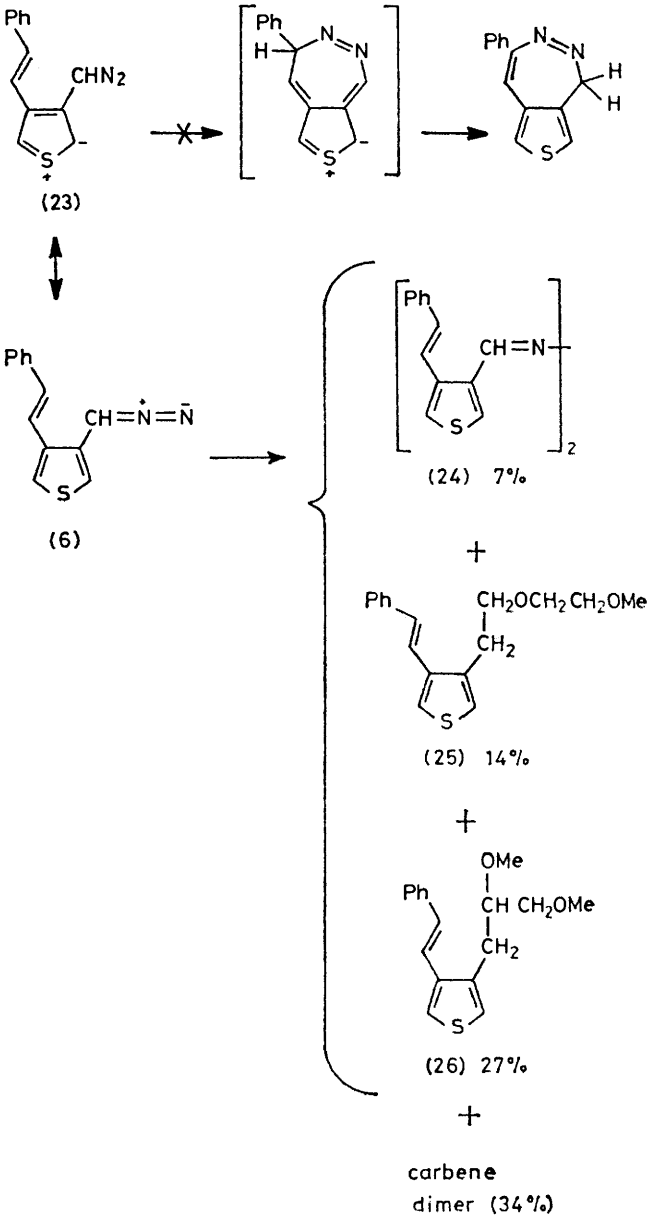
(20)



(10) (21)



(11) (22)



The thieno[3*H*-1,2]diazepines (10) and (11) were readily converted into the diazetothienopyrroles (21) and (22) respectively in quantitative yield on exposure to

daylight or u.v. radiation. Again the product structures were deduced by comparison of their spectra with those of the benzo-analogues.[3]

Although the diazo-compounds (4) and (5) cyclised readily to give diazepines the analogous compound (6) did not. We had hoped that there would be sufficient π-electron delocalisation in thiophen to make the double-bond character of the 3,4-bond high enough to allow the electrocyclic ring closure to proceed as shown formally for one of the dipolar canonical forms (23), but in the reaction the red colour of the diazo-compound persisted for much longer than with (4) or (5) and it gave typical aryl carbene products: the azine (24), solvent insertion products (25) and (26), and material which from its mass spectrum appears to be a carbene ' dimer '.

The cyclisations of diazo-compounds of types (4) and (5) thus provide a route to the new heterocyclic systems the thieno[3,2-*d*]- and thieno[2,3-*d*]-[1,2]diazepines (10) and (11). The substituent patterns of these diazepines should be capable of considerable variation by straightforward modification or extension of the synthetic pathways shown in Schemes 1 and 2.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on a Varian HA 100 spectrometer and ^{13}C n.m.r. spectra on a Varian CFT 20 spectrometer. Chemical shifts are recorded as p.p.m. downfield from internal tetramethylsilane. In the variable-temperature experiments the probe temperature was determined from the chemical shift difference between the methylene and hydroxy protons of ethylene glycol. Mass spectra were obtained with an A.E.I. MS 902 (70 eV) using a direct insertion probe.

The ethanol used for the Wittig reactions and for the preparation of the tosylhydrazone salts was dried by the magnesium method,[4] and 1,2-dimethoxyethane was distilled under nitrogen from calcium hydride. Chromatographic separations were carried out by the medium-pressure technique using either 1 000 × 15 or 1 000 × 25 mm columns packed with Merck Kieselgel 60.

4-Phenyl-5H-2,3-benzodiazepine (17) (*with C. D. Anderson*). —A solution of 4-phenyl-1*H*-2,3-benzodiazepine [1] (1.93 g) and sodium ethoxide [from sodium (0.202 g)] in ethanol (100 ml) was boiled under reflux for 3 h. The ethanol was then evaporated under reduced pressure and benzene (100 ml) was added. After washing with water (2 × 50 ml) and drying, the solvent was evaporated under reduced pressure to give *4-phenyl-5H-2,3-benzodiazepine* (1.20 g, 66%), m.p. 108—110 °C (from ethanol) (Found: C, 81.8; H, 5.45; N, 12.7. $C_{15}H_{12}N_2$ requires C, 81.65; H, 5.6; N, 12.7%); δ_H ($CDCl_3$ at 65 °C) 3.56 br (s, 5-CH_2), 7.1—7.5 (7 H, m), and 7.7—8.0 (2 H, m); on heating the δ 3.56 singlet sharpened and on cooling to −50 °C it separated to give a pair of doublets at δ 2.96 and 4.06 (*J* 12.5 Hz), coalescence temperature = 55 ± 2 °C.

3-Formyl-4-(trans-2-phenylethenyl)thiophen Azine.—3-Formyl-4-(*trans*-2-phenylethenyl)thiophen (0.32 g) was dissolved in ethanol (3 ml) and heated to 50 °C. Hydrazine hydrate (0.17 g) was added followed by one drop of concentrated hydrochloric acid. A yellow solid was formed at once; this was crystallised from ethanol to give the azine (0.21 g, 67%), m.p. 195—197 °C (Found: C, 73.3; H, 4.6; N, 6.5. $C_{26}H_{20}N_2S_2$ requires C, 73.6; H, 4.75; N, 6.6%); δ_H (C_6D_6) 8.93 (s, 2 × CH=N) and 7.08—7.86 (18 H, m, aromatic).

Preparation of Formyl-(trans-2-phenylethenyl)thiophens. (i) *3-Formyl-2-(trans-2-phenylethenyl)thiophen* (7).—*3-Methyl-2-(trans-2-phenylethenyl)thiophen.* A solution of sodium ethoxide [from sodium (2.76 g)] in ethanol (45 ml) was added during 30 min to a mixture of benzyltriphenylphosphonium bromide (44.9 g) and 2-formyl-3-methylthiophen (15.0 g) in ethanol (50 ml) maintained at 30 °C. The reaction mixture was then held at 50 °C for 1½ h. The usual work-up and chromatography (alumina, 10 vol % ether in light petroleum) to remove triphenylphosphine oxide gave a brown oil (23.3 g) containing the *cis*- and *trans*-isomers (g.l.c., 2½% OVI, 182 °C). A solution of this oil (23.0 g) and iodine (0.05 g) in heptane (110 ml) was boiled under reflux for 80 min when the *cis*-isomer was <2%. After evaporation the residue was dissolved in chloroform (100 ml) and washed with aqueous sodium thiosulphate (1% w/v; 100 100 ml), then with water and then dried and evaporated under reduced pressure to give a brown oil (21 g). Chromatography (alumina, 10 vol % ether in light petroleum) gave *3-methyl-2-(trans-2-phenylethenyl)thiophen* (10.39 g, 43%), m.p. 52—53 °C (from ethanol) (Found: C, 78.2; H, 6.2. $C_{13}H_{13}S$ requires C, 77.95; H, 6.0%); δ_H ($CDCl_3$) 2.29 (s, Me) and 6.6—7.4 (m, 9 H).

The hexamethylenetetramine salt of 3-bromomethyl-2-(trans-2-phenylethenyl)thiophen. 3-Methyl-2-(*trans*-2-phenylethenyl)thiophen (12.25 g) and benzoyl peroxide (0.25 g) were dissolved in carbon tetrachloride (120 ml) and heated to reflux when a mixture *N*-bromosuccinimide (11.10 g) and benzoyl peroxide (0.25 g) were added in one batch. The mixture was boiled under reflux for 4 h, cooled, and filtered to remove succinimide. Evaporation of the solvent under reduced pressure gave a dark green oil (17.0 g, 98%) which was shown by n.m.r. spectroscopy to contain 3-bromomethyl-2-(*trans*-2-phenylethenyl)thiophen δ 4.58 (CH_2) and several contaminants (5—10%) which were probably materials brominated in the thiophen ring. The whole product and hexamine (8.6 g) in chloroform (70 ml) were boiled under reflux for 2 h. The volume was reduced by one half by evaporation under reduced pressure and ether (30 ml) was added. After standing at room temperature the hexamethylenetetramine salt was filtered off, washed with ether, and dried *in vacuo* (20.3 g, 79%), m.p. 170—171 °C; this product was contaminated with *ca.* 5% of the salt of 5-bromo-3-bromomethyl-2-(*trans*-2-phenylethenyl)thiophen which could not be removed by recrystallisation so the crude material was used for the next stage.

3-Formyl-2-(trans-2-phenylethenyl)thiophen (7). The crude salt from the previous experiment (19.8 g) and aqueous acetic acid (50 vol %, 44 ml) were boiled under reflux with stirring for 2 h; a solution of hydrochloric acid (11.5 ml) in water (17.5 ml) was added and the mixture was boiled for a further 5 min. After cooling the mixture was extracted with ether (3 × 60 ml) and the extract washed with aqueous potassium carbonate (5% w/v) and dried. Evaporation of the solvent under reduced pressure gave a red oil (9.8 g) which was chromatographed (silica, 20 vol % ether in light petroleum) to give (*a*) 5-bromo-3-formyl-2-(*trans*-2-phenylethenyl)thiophen (0.22 g, *ca.* 2%), m.p. 61—62 °C (from propan-2-ol) (Found: C, 53.5; H, 3.1. $C_{13}H_9BrOS$ requires C, 53.3; H, 3.1%); δ_H ($CDCl_3$) 6.97 (d, *J* 15 Hz, styryl H), 7.18—7.55 (6 H, m, aromatic), 7.80 (d, *J* 15 Hz, styryl H), and 9.96 (s, CHO); $\nu_{max.}$ (Nujol) 1 667 cm^{-1} (C=O): and (*b*) 3-formyl-2-(*trans*-2-phenyl-

ethenyl)thiophen (4.9 g, 49%), m.p. 29—32 °C (from methanol) (Found: C, 72.75; H, 4.7. $C_{13}H_{10}OS$ requires C, 72.9; H, 4.7%); δ_H ($CDCl_3$) 7.0—7.55 (8 H, m), 7.90 (d, *J* 16 Hz, styryl H), and 10.10 (s, CHO); $\nu_{max.}$ (Nujol) 1 670 cm^{-1} (C=O). The latter aldehyde was converted into its *p*-tolylsulphonylhydrazone by the usual method [5] in 77% yield, m.p. 143—145 °C (from ethanol) (Found: C, 62.65; H, 4.8; N, 7.3. $C_{20}H_{18}N_2O_2S_2$ requires C, 62.8; H, 4.7; N, 7.3%); δ_H ($CDCl_3$) 2.32 (s, CH_3), 6.78—7.45 (11 H, m), 7.83 (2 H, d, *J* 8 Hz), 8.04 (s, CH=N), and 8.56br (s, NH); $\nu_{max.}$ (Nujol) 3 200 br cm^{-1} (NH).

(ii) *2-Formyl-3-(trans-2-phenylethenyl)thiophen* (8). *2-Bromo-3-(trans-2-phenylethenyl)thiophen.* A solution of sodium ethoxide [from sodium (2.28 g)] in ethanol (60 ml) was added with stirring during 1 h to a mixture of 2-bromo-3-thienylmethyltriphenylphosphonium bromide [6] (50.0 g) and benzaldehyde (10.3 g) in ethanol (100 ml) at room temperature. After 1 h at room temperature and 1 h at 35 °C the usual work-up and chromatography gave an oil (21 g) from which the *trans*-isomer (*ca.* 3 g) crystallised out. The residual oil was isomerised with iodine in boiling heptane (100 ml); g.l.c. (2½% OVI, 190 °C) showed that the *cis*- and *trans*-isomers reached equilibrium after *ca.* 4 h (*trans* : *cis* = 2.5). Work-up and chromatography (alumina, light petroleum as eluant) and a repeated isomerisation of the separated *cis*-isomer gave *2-bromo-3-(trans-2-phenylethenyl)thiophen* (total yield 14.9 g, 58%), m.p. 78—80 °C (from ethanol) (Found: C, 54.6; H, 3.4. $C_{12}H_9BrS$ requires C, 54.35; H, 3.4%); δ_H ($CDCl_3$) 6.8—8.5 (m).

3-Formyl-3-(trans-2-phenylethenyl)thiophen (8). A Grignard reagent was prepared by stirring a mixture of 2-bromo-3-(*trans*-2-phenylethenyl)thiophen (7.0 g) and magnesium (0.72 g) in tetrahydrofuran (20 ml) for 5 h at room temperature followed by 1 h at reflux. Dimethylformamide (2.0 g) was added at room temperature and the mixture was stirred for 12 h. Work-up by hydrolysis with saturated aqueous ammonium chloride (20 ml) and extraction with ether gave after evaporation under reduced pressure a red oil (6.1 g) which was chromatographed (silica, 20 vol % ether in light petroleum) to give (i) 3-(*trans*-2-phenylethenyl)thiophen (0.89 g, 18%), m.p 126—127 °C (from ethanol) (Found: C, 77.2; H, 5.4. $C_{12}H_{10}S$ requires C, 77.35; H, 5.4%); δ_H ($CDCl_3$) 6.88 (d, *J* 16 Hz, 1 H) and 7.0—7.5 (m, 9 H); (ii) 2-formyl-3-(*trans*-2-phenylethenyl)-thiophen (3.10 g, 55%), m.p. 72—73 °C (from ethanol) (Found: C, 72.7; H, 4.7. $C_{13}H_{10}OS$ requires C, 72.9; H, 4.7%), δ_H ($CDCl_3$) 7.07 (d, *J* 16 Hz, 1 H), 7.2—7.6 (m, 7 H), 7.62 (d, *J* 16 Hz, 1 H), and 10.13 (s, CHO); $\nu_{max.}$ (Nujol) 1 652 cm^{-1} (C=O). The aldehyde was converted into its *p*-tolylsylphonylhydrazone by the usual method [5] in 83% yield, m.p. 127—129 °C (from ethanol) (Found: C, 62.6; H, 4.7; N, 7.2 $C_{20}H_{18}N_2O_2S_2$ requires C, 62.8; H, 4.7; N, 7.3%); δ_H ($CDCl_3$) 2.31 (s, Me), 6.86 (d, *J* 16 Hz, styryl H), 7.1—7.4 (10 H, m), 7.72 (2 H, d, *J* 8 Hz), 8.2 (s, CH=N), and 8.34 (s, NH), $\nu_{max.}$ (Nujol) 3 210 cm^{-1} (NH).

(iii) *3-Formyl-4-(trans-2-phenylethenyl)thiophen* (9). *4-Bromo-3-(trans-2-phenylethenyl)thiophen.* A solution of sodium ethoxide [from sodium (0.862 5 g)] in ethanol (45 ml) was added with stirring during 1 h to a solution of 4-bromo-3-formylthiophen [7] (7.0 g) and benzyltriphenylphosphonium bromide (15.9 g) in ethanol (30 ml) at room temperature. The mixture was then heated at 60 °C for 30 min and stirred at room temperature overnight. The usual work-up and chromatography gave a yellow oil (10.2 g), containing the *cis*- and *trans*-isomers (g.l.c., 2.5% OVI, 190 °C). A solution of this oil and iodine (*ca.* 0.1 g) in heptane (50 ml) was boiled under reflux for 10.5 h and worked up to give *4-bromo-3-(trans-2-phenylethenyl)thiophen* (6.5 g, 67%), m.p. 50—52 °C (from ethanol) (Found: C, 54.6; H, 3.4. $C_{12}H_9BrS$ requires C, 54.35; H, 3.4%); δ_H ($CDCl_3$) 7.05 (d, *J* 2 Hz) and 7.16—7.53 (m).

3-Formyl-4-(trans-2-phenylethenyl)thiophen (9). 4-Bromo-3-(*trans*-2-phenylethenyl)thiophen (6.5 g) in ether (20 ml) was cooled to −70 °C and a solution of butyllithium (1.6M in hexane; 17.6 ml) was added with stirring during 5 min. After a further 5 min dimethylformamide (2.8 ml) was added, the reaction mixture was then allowed to warm to room temperature and was stirred overnight. Aqueous ammonium chloride (saturated, 90 ml) was added and the mixture was extracted with benzene (2 × 60 ml). The extract was washed with water, dried, and evaporated under reduced pressure to give a brown oil which was chromatographed (silica, 15 vol % ether in light petroleum) to give (*a*) 3-(trans-2-*phenylethenyl*)*thiophen* (0.34 g), m.p. 126—127 °C identical with the sample obtained above, (*b*) *3-formyl-4-(trans-2-phenylethenyl)thiophen* (2.80 g, 53%), m.p. 107—108 °C (from ethanol) (Found: C, 72.7; H, 4.7 $C_{13}H_{10}OS$ requires C, 72.9; H, 4.7%); δ_H ($CDCl_3$) 6.98 (d, *J* 16 Hz, styryl H), 7.2—7.6 (6 H, m), 7.72 (d, *J* 16 Hz, styryl H), 8.03 (d, *J* 3 Hz, 2-H), and 9.98 (s, CHO); $\nu_{max.}$ (Nujol) 1 680 cm^{-1} (C=O). This compound was converted into its *p*-tolylsulphonylhydrazone by the usual method [5] in 72% yield, m.p. 175—176.5 °C (from ethanol) (Found: C, 62.8; H, 4.7; N, 7.2. $C_{20}H_{18}N_2O_2S_2$ requires C, 62.8; H, 4.7; N, 7.3%); δ_H [$(CD_3)_2CO$] 2.29 (s, Me), 6.91—7.89 (14 H, m), and 8.14 (s, CH=N); $\nu_{max.}$ (Nujol) 3 220 cm^{-1} (NH).

Preparation and Decomposition of the p-*Tolylsulphonylhydrazone Sodium Salts.*—The sodium salts were prepared and dried as described previously [1,5] and decomposed in dry 1,2-dimethoxyethane in the dark under nitrogen. The reactions were continued until t.l.c. showed that all the reactant had been consumed and any red colour due to the diazo-intermediate had been discharged. After cooling the precipitated sodium toluene-*p*-sulphinate was filtered off and the other products isolated as described.

Preparation of Thienodiazepines.—*2-Phenyl-5H-thieno[2,3-d][1,2]diazepine* (11). 2-Formyl-3-(*trans*-2-phenylethenyl)thiophen tosylhydrazone (2.04 g) sodium salt in 1,2-dimethoxyethane (80 ml) was heated at 60—70 °C for 70 min and worked up to give a brown oil. This was chromatographed (silica, 50 vol % ether in light petroleum) to give *2-phenyl-5H-thieno*[2,3-d][1,2]*diazepine* (0.79 g, 65%) as yellow crystals, m.p. 117—119 °C (from propan-2-ol) (Found: C, 68.6; H, 4.35; N, 12.3. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.45; N, 12.4%); δ_H ($CDCl_3$ at 28 °C) 2.84br [d, *J* 10 Hz, 5-H (quasi *ax*)], 6.52br [d, *J* 10 Hz, 5-H (quasi *equ*)], 6.84 (s, 1-H), 7.12 (d, *J* 5 Hz, 8-H), 7.22 (d, *J* 5 Hz, 7-H), 7.3—7.5 (3 H, m, *m*- and *p*-phenyl), 7.82 (2 H, m, *o*-phenyl), the coalescence temperature for the δ 2.84 and 6.52 doublets was 82 ± 10 °C ($\Delta G^{\ddagger} = 68 \pm 2$ kJ mol^{-1}); δ_C ($CDCl_3$), 64.2 (C-5), 108.8 (C-1), 154.4 (C-2), 124.4 (tert.) 125.5, 125.9, 128.5, 128.8, 137.1 (tert.), and 137.3 (tert.).

2-Phenyl-1H-thieno[2,3-d][1,2]*diazepine* (16). 2-Phenyl-5*H*-thieno[2,3-*d*][1,2]diazepine (0.4 g) in 1,2-dimethoxyethane (10 ml) was added to a solution of sodium ethoxide [from sodium (0.040 3 g)] in ethanol (15 ml) and the solution was stirred at 40 °C for 2 h when t.l.c. (silica, 30 vol % ether in light petroleum) showed that reaction was complete. Chromatography (silica, 30 vol % ether in light petroleum) gave a yellow solid (0.323 g) which was crystallised from

ethanol to give 2-*phenyl*-1H-*thieno*[2,3-d][1,2]*diazepine* (0.295 g, 74%), m.p. 133—134 °C (Found: C, 68.7; H, 4.4; N, 12.2. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.45; N, 12.4%); δ_H ($CDCl_3$ at 28 °C) 3.54br (s, 1-CH_2), 6.94 (d, *J* 5 Hz, 8-H), 7.26—7.42 (3 H, m, *m*- and *p*-phenyl), 7.48 (d, *J* 5 Hz, 7-H), 7.74—7.92 (2 H, m, *o*-phenyl), and 8.47 (s, 5-H), on heating to +65 °C the δ 3.54 singlet sharpened and on cooling to −60 °C it separated to give a pair of doublets at δ 2.71 and 4.37 (*J* 13 Hz), coalescence temperature = −7 ± 2 °C ($\Delta G^{\ddagger}$ = 51.8 ± 0.4 kJ mol^{-1}); δ_C ($CDCl_3$) 30.9 (C-1), 151.4 (C-2), 142.7 (C-5), 141.9 (tert.), 135.8, 131.9, 130.0, 128.6, 127.8, and 125.8.

4-*Phenyl*-1H-*thieno*[3,2-d][1,2]*diazepine* (10). 3-Formyl-2-(*trans*-2-phenylethenyl)thiophen tosylhydrazone (6.72 g) sodium salt in 1,2-dimethoxyethane (180 ml) was heated at 70 °C for 30 min and worked up to give a brown oil (4.1 g). This was chromatographed (silica, 10 vol % ether in light petroleum) to give 4-*phenyl*-1H-*thieno*[3,2-d][1,2]*diazepine* (3.47 g, 87%), m.p. 76—77 °C (from propan-2-ol) (Found: C, 68.9; H, 4.4; N, 12.4. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.45; N, 12.4%); δ_H ($CDCl_3$ at 28 °C) 2.59br [d, *J* 10 Hz, 1-H (quasi *ax*)], 6.55br [d, *J* 10 Hz, 1-H (quasi *equ*)], 6.84 (s, 5-H), 7.02 (d, *J* 5 Hz, H-8), 7.28—7.42 (m, *m*- and *p*-phenyl), 7.48 (d, *J* 5 Hz, H-7), 7.74—7.88 (m, *o*-phenyl), on cooling to −20 °C the δ 2.59 and 6.55 doublets sharpened and on heating they broadened and coalesced at 74 ± 10 °C ($\Delta G^{\ddagger}$ = 66 ± 2 kJ mol^{-1}); δ_C ($CDCl_3$) 65.7 (C-1), 106.8 (C-5), 151.9 (C-4), 125.4 (tert.), 126.0, 126.6, 128.6, 128.8, 131.1, 137.0 (tert.), and 137.8 (tert.).

4-*Phenyl*-5H-*thieno*[3,2-d][1,2]*diazepine* (15). 4-Phenyl-1*H*-thieno[3,2-*d*][1,2]diazepine (3.0 g) in 1,2-dimethoxyethane (30 ml) was added to a solution of sodium ethoxide [from sodium (0.31 g)] in ethanol (150 ml) and the solution was stirred at 65 °C for 3½ h when all the starting material had been consumed. Chromatography (silica, 50 vol % ether in light petroleum) gave (i) an intractable brown tar (0.41 g), and (ii) 4-*phenyl*-5H-*thieno*[3,2-d][1,2]*diazepine* (1.16 g, 39%), m.p. 124.5—125.5 °C (from ethanol) (Found: C, 68.8; H, 4.5; N, 12.3. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.45; N, 12.4%); δ_H ($CDCl_3$ at 28 °C) 3.70br (s, 5-CH_2), 7.05 (d, *J* 5 Hz, 8-H), 7.14 (d, *J* 5 Hz, 7-H), 7.30—7.44 (m, *m*- and *p*-phenyl), 7.72—7.92 (m, *o*-phenyl), and 8.46 (s, 1-H); on heating to +60 °C the δ 3.70 singlet sharpened and on cooling to −55 °C it separated into a pair of doublets at δ 3.05 and 4.44 (*J* 14 Hz), coalescence temperature = −1 ± 2 °C ($\Delta G^{\ddagger}$ = 53.4 ± 0.4 kJ mol^{-1}); δ_C ($CDCl_3$) 30.2 (C-5), 150.9 (C-4), 144.8 (C-1), 140.6 (tert.), 135.6 (tert.), 130.1, 128.7, 127.7, 126.0, and 124.7.

Thermal decomposition of the sodium salt of 3-*formyl*-4-(trans-2-*phenylethenyl*)*thiophen tosylhydrazone*. The tosylhydrazone (1.02 g) sodium salt in 1,2-dimethoxyethane (40 ml) was boiled under reflux for 40 min; initially a red colour developed which then faded to leave a yellow solution and white precipitate. The usual work-up gave a brown oil shown by t.l.c. (silica, 15 vol % ether in light petroleum) to contain five components. Chromatography (silica, graded elution 5 vol % to 10 vol % ether in light petroleum) gave (i) pale yellow crystals, m.p. 107—122 °C (0.18 g); *m/e* 396 (100), 305 (57), 271 (27), 227 (12), 197 (15), 165 (15), and 115 (25%); δ_H 6.44—7.50 (m), (ii) bis-3-formyl-4-(*trans*-2-phenylethenyl)thiophen azine (0.08 g, 7%), m.p. 193—196 °C (from ethanol), identical with an authentic sample, (iii) 3-(2,3-dimethoxypropyl)-4-(*trans*-2-phenylethenyl)thiophen (0.21 g, 27%) as a yellow oil which decomposed on attempted distillation (Found: M^+ 288.116 733. $C_{17}H_{20}O_2S$ requires *M*, 288.118 394); δ_H ($CDCl_3$) 2.90 (d, *J* 7 Hz, propyl 1-CH_2), 3.30 (s, OMe), 3.38 (s, OMe) partly superimposed on δ 3.62 (m, propyl CH and CH_2), 6.96—7.60 (9 H, m); *m/e* 288 (100), 243 (30), 211 (67), 200 (15), 199 (12), 197 (12), 184 (7), 185 (10), and 165 (25%); (iii) 3-[2-(2-methoxyethoxy)ethyl]-4-(*trans*-2-phenylethenyl)thiophen (0.11 g, 14%) as a yellow oil (Found: M^+ 288.117 285. $C_{17}H_{20}O_2S$ requires 288.118 394); δ_H ($CDCl_3$) 2.99 (t, *J* 7 Hz, ethyl 1-CH_2), 3.34 (s, OMe), 3.45—3.65 (4 H, m) partly superimposed on 3.70 (t, *J* 7 Hz, CH_2), 6.93—7.50 (9 H, m); *m/e* 288 (100), 243 (4), 213 (26), 212 (51), 211 (34), 200 (15), 199 (16), 197 (16), 184 (20), and 165 (29).

Photolysis of Thienodiazepines (10) *and* (11).—Irradiation was carried out through Pyrex at 0 °C under nitrogen with a 100 W Hanovia medium-pressure lamp. The yields were essentially quantitative (t.l.c. and n.m.r.) and the products obtained by evaporation of the solvent *in vacuo* at room temperature and drying at *ca.* 0.1 mmHg were analytically pure; attempted recrystallisation from ethanol resulted in decomposition.

2-*Phenyl*-5H-*thieno*[2,3-d][1,2]*diazepine* (11). The diazepine (0.2 g) in cyclohexane (60 ml) was irradiated for 30 min to give 4,7b-*dihydro*-1-*phenyldiazeto*[1,4-a]*thieno*[3,2-c]*pyrrole* (22) (0.195 8 g, 98%), m.p. 120—121.5 °C (Found: C, 68.7; H, 4.4; N, 12.2. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.35; N, 12.3%); δ_H (C_6D_6) [assignments refer to structure (22)] 4.18br (d, *J* 14 and *ca.* 3 Hz, 4-H), 4.37 (d of d, *J* 14 and 3 Hz, 4′-H), 5.68 (t, *J* 3 Hz, 7b-H), 6.49 (d, *J* 5 Hz, 7-H), 6.75 (d, *J* 5 Hz, 6-H), 6.90—7.12 (3 H, m, *m*- and *p*-phenyl), and 7.32—7.45 (2 H, m, *o*-phenyl).

4-*Phenyl*-1H-*thieno*[3,2-d][1,2]*diazepine* (10). The diazepine (0.155 g) in cyclohexane (110 ml) was irradiated for 10 min to give 2a,6-dihydro-2-phenyldiazeto[1,4-*a*]thieno-[2,3-*c*]pyrrole (21) (0.151 g, 97%), m.p. 94.5—95.5 °C (Found: C, 68.8; H, 4.4; N, 12.7. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.35; N, 12.3%); δ_H (C_6D_6) [assignments refer to structure (21)] 4.14 (d of d, *J* 15 and 2 Hz, 6-H), 4.34 (d of d, *J* 15 and 3 Hz, 6′-H), 5.80br (t, *J* 2—3 Hz, 2a-H), 6.27 (d, *J* 5 Hz, H-5), 6.80 (d, *J* 5 Hz, H-4), and 6.92—7.47 (5 H, m, phenyl).

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