1,7-Electrocyclisation and Carbene Reactions of *o*-Alkenylaryldiazoalkanes: The Effect of Alkene Configuration on the Mode of Reaction [1]

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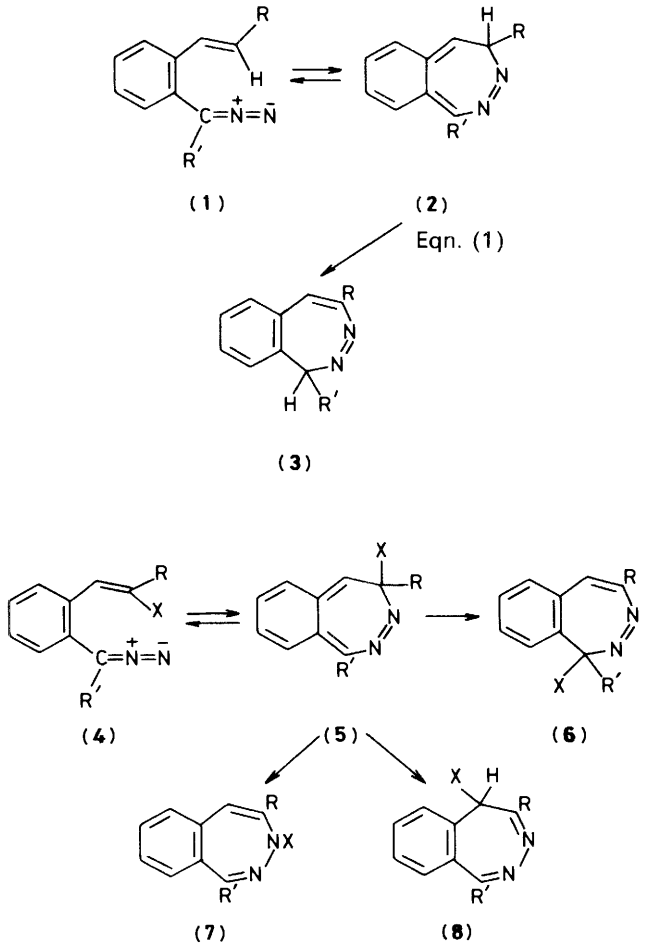
The 1,7-8π-electron electrocyclisation of *o*-alkenylaryldiazoalkanes (**1**) to give 1*H*-2,3-benzodiazepines (**3**) takes place readily for substrates with a *cis*-hydrogen atom at the cyclisation site, but is blocked by phenyl or methyl groups at that position. Such compounds react only *via* loss of nitrogen, the former, *e.g.* (**18**), to give naphtho[*a*]cycloheptenes (**20**) by a new intramolecular carbene reaction, and the latter to give carbene 'dimers', azines, products of solvent insertion, and in one case an indene (**37**). The blocking effect of *cis*-methyl and -phenyl groups is attributed to steric hindrance in a helical transition state (**42**) for the 1,7-electrocyclisation. The results are also discussed in relation to the two possible primary processes of 1,7-electrocyclisation and 1,1-cycloaddition in the reactions of the isoelectronic systems (**43**) and (**47**) containing nitrilium and diazonium betaines.

We have shown in earlier work [2] that diazo compounds of type (**1**) undergo rapid thermal ring closure to give 1*H*-2,3-benzodiazepines (**3**) in high yield [equation (1)]. This principle has also been applied to the synthesis of 3*H*-1,2-diazepines fused to five-membered heteroaromatic rings,[3] to 3*H*-1,2-benzodiazepines,[4,5] and more recently to monocyclic 3*H*-1,2-diazepines.[6] The formation of compounds (**3**) from (**1**) is thought to take place *via* two steps, an 8π-electron 1,7-electrocyclisation to give the intermediate (**2**) followed by a [1,5]-sigmatropic hydrogen shift. A mechanistic study on a related reaction which involves cyclisation at an aromatic rather than an olefinic carbon atom has shown that the cyclisation step is an equilibrium and that the second step is a wholly intramolecular migration.[7]

In the earlier work it had been shown that the efficiency of the cyclisation was affected little by the nature of R and R′ in (**1**), but in all cases studied the substrates had a *cis*-hydrogen atom at the cyclisation site which could migrate in the second step of the reaction. The objective of this work was to examine the reactions of the diazo compounds (**4**) of the same type without such a hydrogen atom but having instead a group X which it was hoped would undergo either [1,5]-migration (suprafacial on X) to give the 1*H*-benzodiazepine (**6**) or [1,7]-migration (antarafacial on X) to give the 3*H*- (**7**) or 5*H*-analogue (**8**) (Scheme 1). The 5*H*-system (**8**) is known to be more thermodynamically stable than the 1*H*-system (**3**).[1] The hypothesis that such migrations would occur was encouraged by the known rapidity of hydrogen shifts in monocyclic 3*H*-1,2-diazepines[8] ($k \simeq 1 \times 10^{-4}$ s^{-1} at 0 °C) and reports that groups other than hydrogen migrate readily in 3*H*-pyrazoles (**10**) to give the 4*H*- (**9**) and/or 1*H*-analogue (**11**) [equation (2)] at temperatures similar to or below that used in the cyclisation of (**1**).[4,9] It was also known that ester and acyl groups in (**10**) show a strong, but not well understood, propensity for migration to N rather than to C and it was of interest to find out if this also occurred in (**5**).

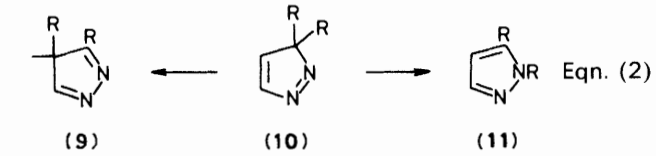


Scheme 1.

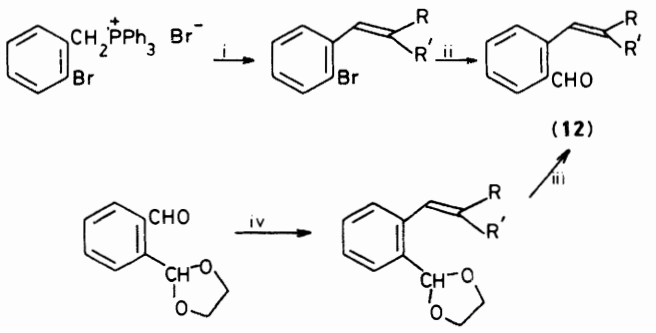
Results and Discussion

(i) *Preparation of Diazo Compound Precursors.*—The diazo compounds were generated *in situ* by the decomposition of the sodium salts of tosylhydrazones at *ca.* 80 °C under aprotic conditions. The aldehydes (**12**) and ketones required for the preparation of the tosylhydrazones were synthesised by routes based on those in Scheme 2. In cases where R ≠ R′ the (*E*)- and (*Z*)-isomers were separated at whatever stage was best favoured by their chromatographic properties.

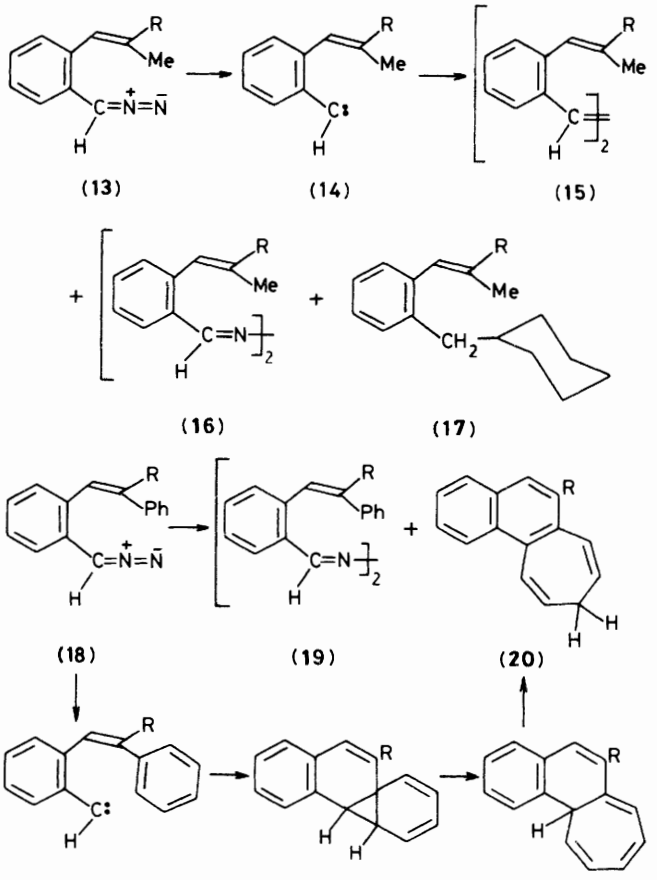
(ii) *Decomposition of the Tosylhydrazone Sodium Salts.*—The initial experiments were carried out with the diazo compounds (**13**; R = Me) and (**18**; R = Ph) carrying two similar substituents at the terminus of the alkenyl group (Scheme 3). Neither gave any benzodiazepines and reacted only *via* loss of nitrogen to give carbene-derived products. Thus, compound (**13**; R = Me) gave the carbene 'dimer' (**15**; R = Me) (40%) and the azine (**16**; R = Me) (38%), formed by reaction of the



(9) (10) (11)

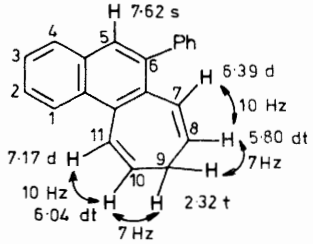


Scheme 2. *Reagents:* i, base, RR'CO; ii, Mg, DMF; iii, H^+/H_2O; iv, $(EtO)_2P(O)CHRR'$, base



Scheme 3.

carbene (**14**) with (**13**), together with the cyclohexyl derivative (**17**; R = Me) (11%) resulting from inserion of (**14**) into the solvent; all of these are well known carbene reactions. The diphenyl analogue (**18**; R = Ph) similarly gave the azine (**19**; R = Ph) (29%), but also the tricyclic compound (**20**; R = Ph) (47%), formed by a new intramolecular carbene reaction, most likely *via* the intermediates shown. The product was formulated as a 9*H*-cyclohepta[*a*]naphthalene on the basis of its elemental analysis and its mass and n.m.r. spectra. The ^1H n.m.r. spectrum at 360 MHz was particularly useful and the chemical shifts and coupling constants, confirmed by decoupling experiments, are shown in structure (**21**).

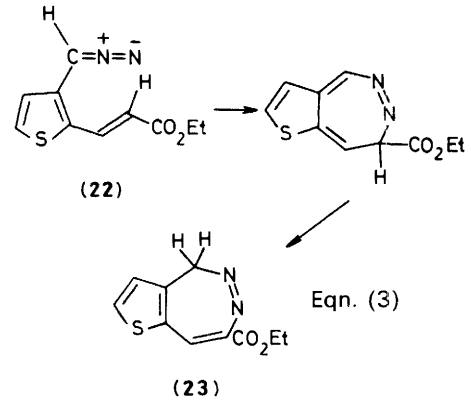


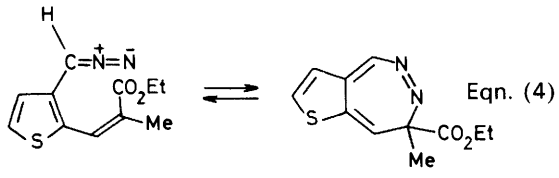
(21)

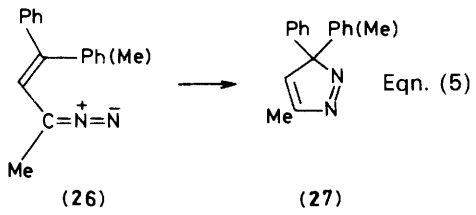
The failure of compound (**13**; R = Me) to give a diazepine was not unexpected since methyl groups have a very low mobility in sigmatropic shifts and it was deduced that this had so much slowed any forward reaction of the postulated intermediate (**5**; R = X = Me) that the diazo compound had reacted instead by loss of nitrogen, which is always competitive with concerted reactions of the diazo group. However the failure of the diphenyl analogue (**18**; R = Ph) to give a diazepine *via* the migration of a phenyl group in (**5**; R = X = Ph) was more surprising in view of the much higher sigmatropic mobility of phenyl, and led us towards the synthesis of diazo compounds, *e.g.* (**4**; X = CO_2Et or COPh, R = Me), carrying ester and benzoyl groups which have a mobility comparable with that of hydrogen.

Diazo compounds of type (**1**; R = ester or acyl) had not previously been cyclised and it was decided to study these first to check both on the success of the cyclisation for substrates with an electron-withdrawing group at the cyclisation site, and on the stability of ester and acyl substituted benzodiazepines. In such cyclisations the intermediate [*e.g.* (**2**; R = COPh)] could in principle react *via* a [1,7]-shift of PhCO or a [1,5]-shift of either H or PhCO, but since it will adopt a preferred conformation with the bulkier acyl group in the pseudo-equatorial position,[2] the H is the more likely to participate in a [1,5]-migration. The tosylhydrazone salt precursors for compounds (**1**; R' = H, R = CO_2Et) and (**1**; R' = H, R = COPh) decomposed in the usual way, but both gave multi-component product mixtures from which no pure materials were isolated. However, the analogous thiophene system (**22**) gave the diazepine (**23**) (76%) in good yield *via* the expected hydrogen shift [equation (3)]. The product was identified by comparison of its ^1H and ^{13}C n.m.r. spectra with those of similar systems.[2,3] The analogous diazo compound (**24**) having a methyl and an ester group at the cyclisation site did not cyclise, and like compounds (**13**) and (**18**) gave only carbene-derived products; the dimer analogous to (**15**) was obtained in 15% yield when the reaction was carried out in cyclohexane, and the reaction in cyclohexene gave an isomeric mixture (62%) containing predominantly the carbene–cyclohexene adduct together with some insertion product. Since the methyl group is bulkier than the ester group[10] the conformation of the postulated intermediate (**25**) [equation (**4**)] having the ester group in the pseudoaxial position should be well populated enough for [1,5]-ester migration to be possible as well as [1,7].

This complete failure of all the diazo compounds (**13**), (**18**), and (**24**) to undergo conversion into diazepines raised the

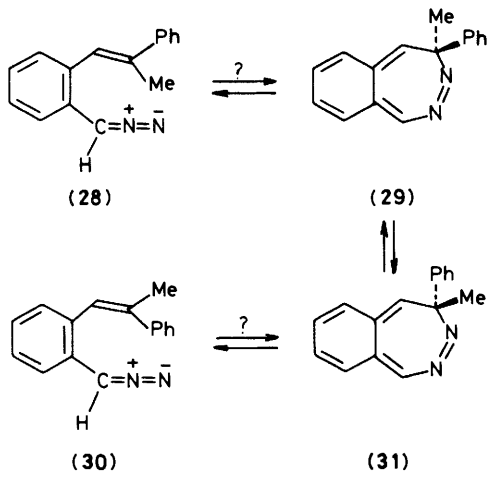




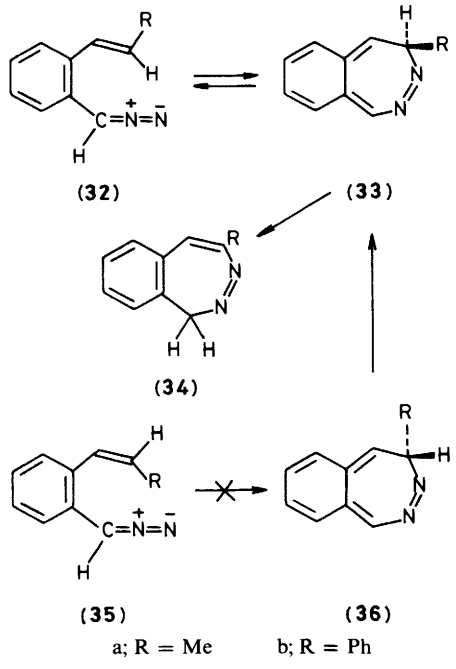


possibility that the blockage of the cyclisation might be due, not to the reluctance of Me, Ph, and CO_2Et to migrate in the second step, but instead to their inhibition of the ring-closure step by steric hindrance. This had originally been thought to be unlikely since it was known that such substituents do not inhibit the 1,5-electrocyclisation of α,β-unsaturated diazo compounds to 3*H*-pyrazoles, *e.g.* (**26**) into (**27**) [equation (5)].[4,11]

Two different experimental tests of this hypothesis were carried out. The first required the generation and decomposition of the (*E*)- and (*Z*)-isomers (**28**) and (**30**). If, as shown in Scheme 4, the ring-closure step were not inhibited, then these substrates would be in equilibrium with the intermediates (**29**) and (**31**), respectively, which are interconvertible by ring inversion.* The activation energy for such inversion is likely to be low [*cf.* the $\Delta G^{\ddagger}$ for the isolated diazepine systems (**3**) and (**23**) is *ca.* 65—72 kJ mol^{-1}] and it would therefore be expected that the more hindered intermediate (**31**; Ph pseudoaxial) would be converted into the more stable conformation (**29**). Thus, the postulated equilibria with the intermediates would provide a route for the isomerisation of (**30**) into (**28**). The results, however, exclude any such isomerisation; the (*E*)-isomer (**28**) gave the azine (**16**; R = Ph) (81%) as the only isolated product and the (*Z*)-isomer (**30**) gave 6-methyl-9*H*-cyclohepta[*a*]naphthalene (**20**; R = Me) (76%) and the azine (**19**; R = Me) (11%) in which the original stereochemistry of the alkene was preserved. This result therefore suggests that both *cis*-Me and *cis*-Ph block the cyclisation step and the intermediates (**29**) and (**31**) are not formed. This was confirmed by experiments using the (*E*)- and (*Z*)-isomers (**32a**) and (**32b**) and (**35a**) and (**35b**) of substrates monosubstituted at the cyclisation site. Thus, both of the (*E*)-



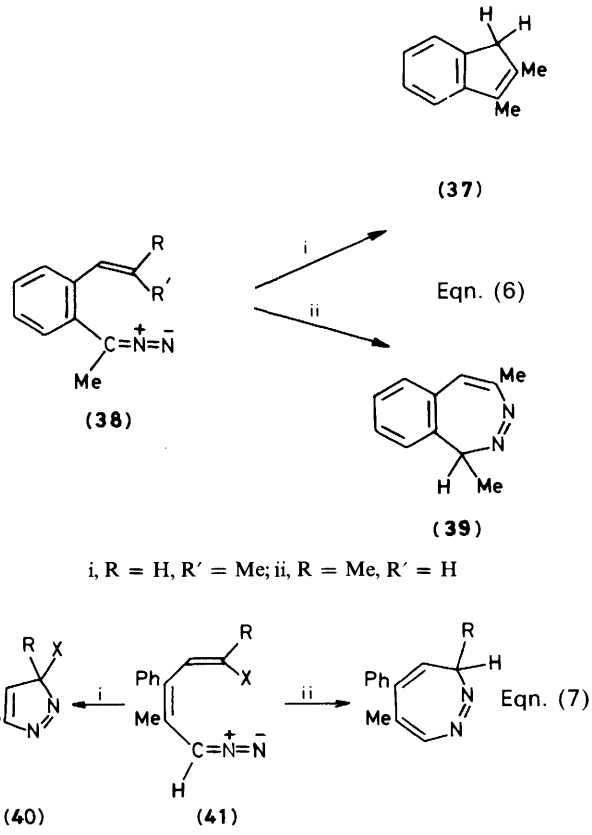
Scheme 4.



Scheme 5.

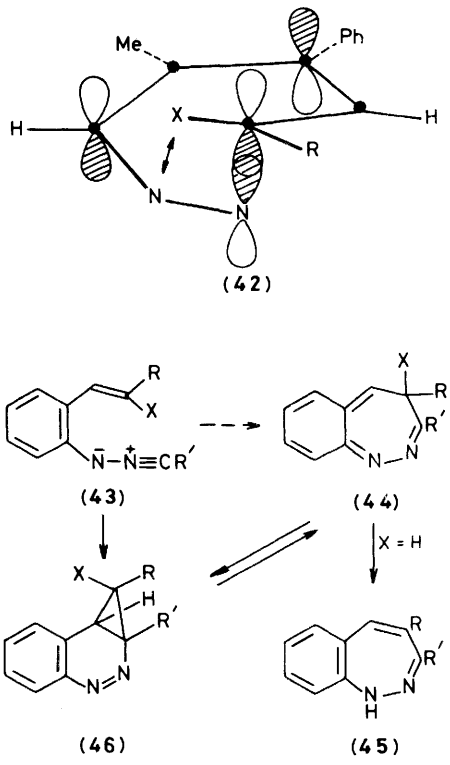
isomers (**32a**) and (**32b**) gave the benzodiazepines (**34a**) and (**34b**) in high yield [76 and 85% respectively (Scheme 5)] whereas the (*Z*)-isomers (**35a**) and (**35b**) produced no detectable trace of the diazepines (t.l.c. monitoring) and decomposed much more slowly to give only products derived from carbenes.This result confirms the suggestion that the presence of the *cis*-methyl or -phenyl group in (**35a**) and (**35b**) prevents the formation of the intermediate (**36**). This, if formed, would be expected to undergo an easy conversion into the benzodiazepine (**34**) *via* ring inversion to the more stable conformer (**33**).* The carbene products were as expected; (**35a**) gave the azine (**16**; R = H) (49%) and the inserion product (**17**; R = H) (15%) while (**35b**) gave the azine (**19**; R = H) (28%), the solvent insertion product (10%), and the cyclohepta[*a*]-naphthalene (**20**; R = H) (42%). Further confirmation was obtained from the reactions of the analogous diazo compounds

* The conformational assignments of the proximate products (**29**) and (**31**) [and also (**33**) and (**36**)] are based on a transition state for ring closure of the type shown in (**42**).



i, R = H, R′ = Me; ii, R = Me, R′ = H

i, X = Me or Ph; ii, X = H



Scheme 6.

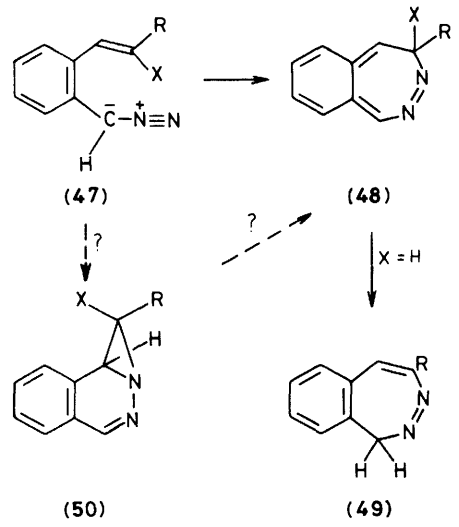
(38; R,R′ = H and Me) derived from (*E*)- and (*Z*)-*o*-acetyl-β-methylstyrenes [equation (6)]. The (*E*)-isomer again gave the benzodiazepine (**39**) (89%) while the (*Z*)-isomer gave only carbene products, in this case a mixture of hydrocarbons containing predominantly (>90%) 2,3-dimethylindene (**37**) as shown by comparison of its ^{1}H n.m.r. spectrum with literature data.[12] Interestingly, the substitution of a methyl group at the carbene centre has again produced the strong promoting effect on intramolecular carbene cyclisation that we pointed out recently.[13]

These results show that the presence of a *cis*-methyl or a *cis*-phenyl group at the cyclisation site of 2-alkenylaryldiazoalkanes (**4**; X = Me or Ph) effectively blocks the 1,7 ring-closure reaction which is the dominant reaction path for the analogues (**1**) with a *cis*-hydrogen atom. Since this work was completed it has been shown that this is also true for the 1,7-cyclisation of diazo compounds with only olefinic α,β and γ,δ unsaturation,[6] *e.g.* (**41**) [equation (7)]. However, in that case when X is methyl or phenyl the diazo compound is diverted mainly into the 1,5-electrocyclisation reaction giving the 3*H*-pyrazoles (**40**) rather than exclusively into carbene reactions as above.

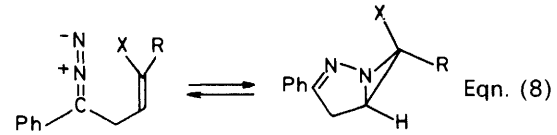
To explain this blocking effect on the 1,7-cyclisation, it is necessary to consider the mechanism and nature of the transition state for the ring-closure step. We have postulated that it is an 8π-electron 1,7-electrocyclisation process and have recently suggested[6] that the transition state for the analogous system with olefinic α,β and γ,δ double bonds is of the form shown in structure (**42**). Such a transition state brings the terminal atoms into a bonding overlap and requires no angular distortion at the trigonal carbon atoms and the minimum distortion of the diazo group from its preferred linear geometry.[14,15] In such a transition state, the steric interaction [↔ in (**42**)] between the *cis* group X and N-2 of the diazo group is small when X = H, but models show that the larger *cis*-methyl or -phenyl groups come into significant steric interaction with N-2. This would raise the energy of the transition state either by inhibiting overlap between the orbitals at the two reacting termini or by causing the terminal carbon atom to twist so that the conjugation required for an electrocyclisation process would be lost. This rationalisation is also applicable to systems (**1**) and (**4**).

However, in view of work carried out elsewhere on related systems the question of whether 1,7-electrocyclisation *is* the primary step in the conversion of compound (**1**) into (**3**) has to be raised. Nitrilium betaines, isoelectronic with (**1**), undergo reactions which are in some respects very similar. Thus, the nitrile imines (**43**; R or X = H), when heated at 80 °C, readily undergo cyclisation to give the 1*H*-1,2-benzodiazepine system (**45**).[16,17] This conversion also depends on the presence of a hydrogen atom on the terminal carbon atom of the alkene, but unlike the diazo system it may be in either the *cis* or *trans* position. When the imine (**43**) is generated at room temperature, however, it reacts to give the cyclopropa[*c*]cinnoline system (**46**) *via* a highly stereospecific 1,1-cycloaddition process which is not inhibited by the presence of *cis*-methyl[17] or -phenyl[18] groups (Scheme 6). Heating compound (**46**) at 80 °C effects the conversion into the benzodiazepine system (**45**) provided X or R is hydrogen. The reactions of the nitrile imine *can* thus be rationalised on the basis of a primary 1,1-cycloaddition step giving (**46**) rather than a 1,7-electrocyclisation giving (**44**).

In view of this, the possibility has to be considered that the conversion of the diazo compound (**47**) into the 2,3-benzodiazepine (**49**) (Scheme 7) also goes *via* a primary 1,1-cycloaddition to give the bridged intermediate (**50**), followed by electrocyclic ring opening to give the 4*H*-benzodiazepine (**48**) and finally a [1,5]-hydrogen shift giving the isolated product. This is particularly important since recent work[19–21] has shown that diazo compounds *can* react *via* stereospecific 1,1-cycloadditions, *e.g.* (**51**) gives the cyclopropapyrazole (**52**) when kept at room temperature for several hours [equation (8)]. At



Scheme 7.



(51) (52)

80 °C, however, the reaction is reversed and so we would not expect to isolate the analogous species (**50**) from the reactions of the diazo compounds (**47**; R or X ≠ H) which were all carried out at 80 °C. This does not rule out 1,1-cycloaddition as the primary step in Scheme 7 when R or X = H; however, there is no positive support for such a process and it conflicts with some of the results presented in this paper, particularly those of the reactions of the (*E*)- and (*Z*)-isomers (**32**) and (**35**). The 1,1-cycloadditions of the nitrile imines (**43**) and of analogous nitrile ylides[22] are not inhibited by the presence of *cis*-methyl or -phenyl groups and similarly the 1,1-cycloadducts (**52**; X = Me, R = H or Me) have been prepared from diazo compounds having X = Me.[20,21] That being so one would expect similar characteristics for a 1,1-cycloaddition of compound (**47**) so that, for example, the (*E*)- and (*Z*)-isomers (**32a**) and (**35a**) should give (**50**; X = H, R = Me) and (**50**; X = Me, R = H), respectively. Since it is found that only the (*E*)-isomer gives the benzodiazepine (**34**; R = Me), this hypothesis would require that the *exo*-isomer (**50**; X = H, R = Me) undergoes ring opening to give the 4*H*-benzodiazepine (**48**) while the *endo*-isomer (**50**; X = Me, R = H) does not. This would be difficult to justify in view of the fact that both the *exo*- and *endo*-isomers of the analogous bridged compound (**46**; R and X = H and Me) are readily converted into (**45**; R = Me) on being heated at 80 °C and undergo *endo*→*exo* isomerisation *via* the 4*H*-benzodiazepine (**44**) at lower temperatures.[17] Thus, if 1,1-cycloaddition *is* the primary process in the conversion of the diazo compound (**47**) into the 1*H*-benzodiazepine (**49**) it must be much more sensitive to steric hindrance in this case than in the conversion of the aliphatic analogue (**51**) into the cyclopropapyrazole (**52**) and in the reactions of the nitrile imine (**43**).*

Experimental

^{1}H N.m.r. spectra were obtained on Varian EM360 (60 MHz) and HA100 (100 MHz) or Bruker WH360 (360 MHz) spectrometers, and ^{13}C n.m.r. spectra on a Varian CFT20 (25 MHz) instrument. All samples were run as solutions in deuteriochloroform unless otherwise stated and chemical shifts are recorded as δ values.

Mass spectra were obtained using an AEI MS902 instrument operated at 70 eV. Preparative column chromatography on silica was carried out by the medium pressure technique[23] (< 100 p.s.i.) using either 1 000 × 15 or 1 000 × 25 mm columns packed with Merck Kieselgel 60. Eluting solvents were based on light petroleum, b.p. 40—60 °C, with varying proportions of diethyl ether. Column chromatography on alumina used material from Laporte Industries (Grade H, 100/200 mesh) deactivated to Grade III, and gravity elution. 'Evaporation' of solvents indicates evaporation under reduced pressure using a rotary evaporator.

Reagents and Starting Materials.—1,2-Dimethoxyethane (DME), cyclohexane, and tetrahydrofuran were freshly distilled from calcium hydride as required. Diethyl ether (referred to as ether) was distilled from lithium aluminium hydride and cyclohexene was distilled and stored over sodium wire. The following compounds were prepared by literature methods: 3-formylthiophene,[24] thiophene-3-carbaldehyde ethylene acetal,[25] 2-formylthiophene-3-carbaldehyde ethylene acetal,[26] diethyl ethoxycarbonylmethylphosphonate,[27,28] diethyl 1-ethoxycarbonylethylphosphonate,[27,29] 2-bromobenzaldehyde ethylene acetal,[30] and 2-formylbenzaldehyde ethylene acetal,[31] which had b.p. 81 °C at 0.1 mmHg (no value reported [31]) and δ_H (100 MHz) 4.04 (4 H, br s, CH_2CH_2), 6.31 (1 H, s, CH), 7.28—7.91 (4 H, m, aromatic), and 10.39 (1 H, s, CHO).

Preparation of 1-*Acetyl- and* 1-*Formyl*-2-*alken*-1-*ylbenzenes and Their Tosylhydrazones.*—The Wittig reactions and the reactions of Grignard reagents with *N,N*-dimethylformamide which are used in most of these synthesis are described in detail only for the first example. The tosylhydrazones of the aldehydes were prepared by admixture of warm (45 °C), ethanolic, equimolar solutions of the aldehyde and toluene-*p*-sulphonohydrazide after which the solution was left at room temperature overnight to crystallise.

(i) (E)- *and* (Z)-*Isomers of* 1-*formyl*-2-(2-*phenylethenyl*)-*benzene.* A solution of sodium ethoxide [(0.2 mol) from sodium (4.5 g)] in ethanol (200 ml) was added during 1 h to a stirred mixture of benzaldehyde (21.0 g, 0.195 mol) and 2-bromobenzyltriphenylphosphonium bromide (100.0 g, 0.195 mol) in ethanol (200 ml) at room temperature. The mixture was stirred at room temperature overnight. Evaporation of the solvent followed by short column chromatography (alumina, light petroleum) to remove the triphenylphosphine oxide gave an oil containing a mixture of (*E*)- and (*Z*)-isomers. Chromatography (silica, light petroleum), monitored by g.l.c. (3% OVI, 190 °C), gave (i) (Z)-1-*bromo*-2-(2-*phenylethenyl*)*benzene* (21.1 g, 39%), b.p. 98 °C at 0.2 mmHg (Found: C, 64.6; H, 4.3. $C_{14}H_{11}Br$ requires C, 64.9; H, 4.3%); δ_H (100 MHz) 6.60 (2 H, s, CH=CH), 6.90—7.20 (8 H, m), and 7.52 (1 H, m); and (ii) a mixture of (*Z*)- and (*E*)-isomers (1:1) (23.0 g). The latter was isomerised to give the (*E*)-isomer (> 95% by g.l.c.) by heating under reflux in n-heptane (100 ml) containing iodine (0.05 g) for 56 h. Evaporation of the solvent under reduced pressure and distillation gave (*E*)-1-bromo-2-(2-phenylethenyl)benzene (20.9 g, 38%), b.p. 115 °C at 0.15 mmHg (lit.,[32] 145 °C at 0.55 mmHg).

To the Grignard reagent prepared from 1-bromo-2-(2-phenylethenyl)benzene (20.0 g, 0.077 mol) and magnesium (2.0 g, 0.08 g-atom) in tetrahydrofuran (70 ml) was added a solution of dimethylformamide (10.0 g, 0.13 mol) in tetrahydrofuran (50 ml) during 30 min. The mixture was allowed to cool to room temperature and a solution of ammonium chloride (200 ml; 25%

* See note on p. 857.

w/v) was added. Extraction with ether, washing with water, drying, and evaporation of the solvents under reduced pressure gave a yellow oil (15.8 g) which, on distillation, gave (Z)-1-*formyl*-2-(2-*phenylethenyl*)*benzene* (12.8 g, 80%), b.p. 87 °C at 0.2 mmHg (Found: C, 86.5; H, 5.9. $C_{15}H_{12}O$ requires C, 86.5; H, 5.8%); δ_H (100 MHz) 6.68 (1 H, d, *J* 11 Hz, PhCH=), 6.90 (1 H, d, *J* 11 Hz, =CHAr), 6.90—7.40 (8 H, m, aromatic), 7.79 (1 H, m, aromatic), and 10.18 (1 H, s, CHO); $\nu_{max.}$(film) 1 690 cm^{-1} (C=O. *Tosylhydrazone* (79%), m.p. 104.5—106 °C (from ethanol) (Found: C, 70.4; H, 5.5; N, 7.5. $C_{22}H_{20}N_2O_2S$ requires C, 70.2; H, 5.4; N, 7.4%); $\nu_{max.}$(Nujol) 3 160 cm^{-1} (NH).

A similar procedure using (*E*)-1-bromo-2-(2-phenylethenyl)-benzene gave (*E*)-1-formyl-2-(2-phenylethenyl)benzene (67%), m.p. 79—80 °C (lit.,[33] 83 °C). Tosylhydrazone (73%), m.p. 142—144 °C (from ethanol) (lit.,[2] 145—146 °C); $\nu_{max.}$(Nujol) 3 210 cm^{-1} (NH).

(ii) 1-*Formyl*-2-(2-*methyl*-2-*phenylethenyl*)*benzene as a mixture of* (E)- *and* (Z)-*isomers*. A Wittig reaction between 2-bromobenzyltriphenylphosphonium bromide (70.0 g, 0.138 mol) and acetophenone (16.5 g, 0.138 mol) as described above gave an oil (30.9 g) shown by g.l.c. (2.5% OVI 190 °C) to contain a *ca.* 1:1 mixture of the (*E*)- and (*Z*)-isomers which was unchanged by treatment with iodine in heptane at reflux. Distillation gave 1-*bromo*-2-(2-*methyl*-2-*phenylethenyl*)*benzene* as an *E*/*Z* mixture (23.4 g, 63%), b.p. 124 °C at 0.5 mmHg (Found: C, 66.2; H, 5.0. $C_{15}H_{13}Br$ requires C, 66.0; H, 4.8%); δ_H (100 MHz) 2.08 (3 H, d, *J* 1.5 Hz, *Z*-Me), 2.20 (3 H, d, *J* 1.5 Hz, *E*-Me), and 6.52—7.66 (10 H, m, aromatic and olefinic). A Grignard reagent from this halide mixture (23.4 g, 0.086 mol) and magnesium (2.05 g, 0.086 g-atom) in ether (100 ml) on reaction with dimethylformamide (12.0 g, 0.11 mol) as described above gave a yellow oil (16.3 g) which on distillation gave 1-*formyl*-2-(2-*methyl*-2-*phenylethenyl*)*benzene* as an *E*/*Z* mixture (2:1) (14.7 g, 77%), b.p. 132 °C at 0.5 mmHg (Found: C, 86.3; H, 6.6. $C_{16}H_{14}O$ requires C, 86.4; H, 6.4%); δ_H (100 MHz) 2.05 (d, *J* 1.5 Hz, *E*-Me) and 2.30 (d, *J* 1.5 Hz, *Z*-Me) (total 3 H, ratio 1:2), 6.90—7.97 (10 H, m, aromatic and olefinic), 10.20 (s, *Z*-CHO), and 10.24 (s, *E*-CHO) (total 1 H, ratio 2:1). This mixture could not be separated by chromatography. Solutions of the mixture (5.0 g, 0.026 mol) in ethanol (20 ml) and of toluene-*p*-sulphonohydrazide (4.2 g, 0.026 mol) in ethanol (20 ml) at 45 °C were mixed and allowed to stand at room temperature for 24 h. Evaporation of the solvent gave a yellow oil (9.2 g) which by chromatography (silica, 50 vol % ether in petroleum) gave (a) (*E*)-1-*formyl*-2-(2-*methyl*-2-*phenylethenyl*)*benzene tosylhydrazone* (4.2 g, 48%), m.p. 124.5—126.5 °C (from ethanol) (Found: C, 70.5; H, 5.6; N, 7.2. $C_{23}H_{22}N_2O_2S$ requires C, 70.8; H, 5.7; N, 7.2%); $\nu_{max.}$(Nujol) 3 240 cm^{-1} (NH); δ_H (100 MHz) 1.90 (3 H, d, *J* 1.5 Hz, Me), 2.32 (3 H, s, tosyl Me), 6.85 (1 H, m, CH=), 7.10—7.85 (13 H, m, aromatic), 7.92 (1 H, s, CH=N), and 8.45 (1 H, br s, NH); and (ii) (Z)-1-*formyl*-2-(2-*methyl*-2-*phenylethenyl*)-*benzene tosylhydrazone* (2.0 g, 23%), m.p. 140—142 °C (from ethanol) (Found: C, 71.0; H, 5.7; N, 7.2. $C_{23}H_{22}N_2O_2S$ requires C, 70.8; H, 5.7; N, 7.2%); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH); δ_H (100 MHz) 2.16 (3 H, d, *J* 1.5 Hz, Me), 2.32 (3 H, s, tosyl Me), 6.54 (1 H, m, CH=), 6.75—7.86 (13 H, m, aromatic), 7.98 (1 H, s, CH=N), and 8.48 (1 H, br s, NH).

(iii) 1-*Formyl*-2-(2-*methylethenyl*)*benzene*. A Wittig reaction between 2-bromobenzyltriphenylphosphonium bromide (200 g, 0.39 mol) and acetaldehyde (16.1 g, 0.37 mol) using the method above gave after chromatography an oil (56.3 g). This was shown by g.l.c. (3% OVI, 120 °C) to be a mixture of (*Z*)- and (*E*)-isomers in the ratio 1:0.65 which was not separable by column chromatography. Distillation gave 1-bromo-2-(2-methylethenyl)benzene as a *E*/*Z* mixture (48.8 g, 69%), b.p. 52 °C at 0.2 mmHg (Found: C, 55.0; H, 4.5. C_9H_9Br requires C, 54.9; H, 4.6%); δ_H (100 MHz) 1.75 (dd, *J* 7 and 1.5 Hz, *Z*-Me) and 1.89 (dd, *J* 7 and 1.5 Hz, *E*-Me (total 3 H, ratio 1:0.65), and 5.7—7.6 (6 H, m, aromatic and olefinic). A sample of this mixture (15 g, 0.076 mol) and iodine (0.1 g) in n-heptane were heated under reflux for 40 h. After evaporation of the solvent the residue was dissolved in chloroform (60 ml), washed with aqueous sodium thiosulphate (3 × 50 ml; 10% w/v), and then with water, dried, and evaporated to give an oil. Chromatography (alumina, light petroleum) followed by distillation gave (E)-1-*bromo*-2-(2-*methylethenyl*)*benzene* (12.1 g, 81%), b.p. 60—63 °C at 0.3 mmHg.

A Grignard reagent prepared from the mixture of (*E*)- and (*Z*)-1-bromo-2-(2-methylethenyl)benzene (30 g, 0.152 mol) and magnesium (4.0 g, 0.165 g-atom) in tetrahydrofuran (80 ml) reacted with dimethylformamide as described above to give a yellow oil (21.9 g). Distillation gave 1-*formyl*-2-(2-*methylethenyl*)*benzene* as an *E*/*Z* mixture (0.6:1) (15.7 g, 71%), b.p. 58 °C at 0.4 mmHg (Found: C, 82.2; H, 7.0. $C_{10}H_{10}O$ requires C, 82.2; H, 6.9%); δ_H (100 MHz) 1.65 (dd, *J* 7 and 1.5 Hz, *Z*-Me) and 1.89 (dd, *J* 7 and 1.5 Hz, *E*-Me) (total 3 H, ratio 1:0.6), 5.80—6.86 (2 H, m, olefinic), 7.11—7.90 (4 H, m, aromatic), 10.14 (s, *Z*-CHO), and 10.20 (s, *E*-CHO) (total 1 H, ratio 1:0.6). This mixture was not separable by column chromatography. A similar reaction using the pure (*E*)-halide (11.5 g, 0.058 mol) gave (*E*)-1-formyl-2-(2-methylethenyl)benzene (7.3 g, 86%), b.p. 45 °C at 0.2 mmHg; δ_H 1.89 (3 H, dd, *J* 7 and 1.5 Hz, Me), 5.79—6.90 (2 H, m, olefinic), 7.11—7.92 (4 H, m, aromatic), and 10.20 (1 H, s, CHO). The (E)-*tosylhydrazone* was prepared in the usual way from the (*E*)-aldehyde (59%), m.p. 125—127 °C (from ethanol) (Found: C, 65.0; H, 5.7; N, 8.7. $C_{17}H_{18}N_2O_2S$ requires C, 65.0; H, 5.8; N, 8.9%); $\nu_{max.}$(Nujol) 3 160 cm^{-1} (NH); δ_H (100 MHz) 1.82 (3 H, dd, *J* 7 and 1.5 Hz), 2.32 (3 H, s, tosyl Me), 5.90 (1 H, dq, *J* 15 and 7 Hz, 2′-H), 6.66 (1 H, dq, *J* 15 and 1.5 Hz, 1′-H), 7.00—7.92 (8 H, m, aromatic), 8.18 (1 H, s, CH=N), and 8.84 (1 H, br s, NH). A mixture of the (*E*)- and (*Z*)-tosylhydrazones was prepared in the usual way from the mixture of *E*/*Z*-aldehydes, but could not be separated by chromatography. Fractional crystallisation from ethanol gave the (*Z*)-tosylhydrazone (15%), m.p. 135—137 °C (from ethanol) (Found: C, 65.2; H, 5.8; N, 9.1. $C_{17}H_{18}N_2O_2S$ requires C, 65.0; H, 5.8; N, 8.9%); $\nu_{max.}$(Nujol) 3 220 cm^{-1} (NH); δ_H (100 MHz) 1.49 (3 H, dd, *J* 7 and 1.5 Hz, Me), 2.35 (3 H, s, tosyl Me), 5.78 (1 H, dq, *J* 10 and 7 Hz, 2′-H), 6.42 (1 H, dq, *J* 10 and 1.5 Hz, 1′-H), 7.00—7.89 (8 H, m, aromatic), 7.92 (1 H, s, CH=N), and 8.53 (1 H, br s, NH).

(iv) 1-*Acetyl*-2-(2-*methylethenyl*)*benzene as a mixture of* (E)- *and* (Z)-*isomers*. To the Grignard reagent prepared from methyl iodide (19.0 g, 0.134 mol) and magnesium (3.5 g, 0.146 g-atom) in tetrahydrofuran (50 ml) was added a solution of the *E*/*Z* mixture of 1-formyl-2-(2-methylethenyl)benzene (18.5 g, 0.127 mol) in tetrahydrofuran (100 ml). The mixture was stirred at room temperature overnight and then a solution of ammonium chloride (200 ml; 25% w/v) was added. Ether extraction, washing with water, drying, and evaporation gave a yellow oil (19.4 g). Distillation gave an *E*/*Z* mixture (0.6:1) of 1-hydroxyethyl-2-(2-methylethenyl)benzene (16.9 g, 82%), b.p. 72 °C at 0.2 mmHg. A similar reaction using (*E*)-1-formyl-2-(2-methylethenyl)benzene gave (E)-1-*hydroxyethyl*-2-(2-*methylethenyl*)*benzene* (78%), b.p. 72 °C at 0.2 mmHg (Found: C, 81.6; H, 8.7. $C_{11}H_{14}O$ requires C, 81.4; H, 8.7%); δ_H (100 MHz) 1.30 (3 H, d, *J* 6 Hz, Me), 1.74 (3 H, dd, *J* 7 and 1.5 Hz, olefinic Me), 3.08 (1 H, br s, OH), 5.02 (1 H, q, *J* 6 Hz, C*H*Me), 5.97 (1 H, dq, *J* 15 and 7 Hz, 2′-H), 6.58 (1 H, dq, *J* 15 and 1.5 Hz, 1′-H), and 7.03—7.45 (4 H, m, aromatic); $\nu_{max.}$(Nujol) 3 350 (OH) and 1 600 cm^{-1} (C=C). Chromium trioxide (9.3 g, 0.094 mol) was added during 15 min with stirring and ice-cooling to pyridine (80 ml). (*E*)-1-Hydroxyethyl-2-(2-methylethenyl)benzene (4.8 g, 0.03 mol) was added and the mixture was stirred at room temperature overnight. Ether (400 ml) was added and the precipitate was filtered off. Water (100 ml) was added to the

filtrate, the ether layer was separated, and the aqueous layer was extracted with ether (2 × 100 ml). The combined ether extract was washed with hydrochloric acid (1M; 3 × 100 ml), aqueous sodium hydrogencarbonate (3 × 100 ml; 20% w/v), water (2 × 150 ml), and dried. Evaporation of the ether gave an oil which was distilled to give (E)-1-*acetyl*-2-(2-*methylethenyl*)-*benzene* (3.38 g, 71%), b.p. 61 °C at 0.2 mmHg (Found: C, 82.7; H, 7.7. $C_{11}H_{12}O$ requires C, 82.5; H, 7.5%); δ_H (100 MHz) 1.82 (3 H, dd, *J* 7 and 1.5 Hz, olefinic Me), 2.49 (3 H, s, Me), 5.91 (1 H, dq, *J* 15 and 7 Hz, 2'-H), 6.84 (1 H, dq, *J* 15 and 1.5 Hz, 1'-H), and 7.10—7.71 (4 H, m, aromatic). A mixture of the (*E*)- and (*Z*-isomers (0.6:1) of 1-acetyl-2-(2-methylethenyl)benzene was prepared by a similar procedure from the *E*/*Z* mixture of the 1-hydroxyethyl derivatives (52%), b.p. 61 °C at 0.2 mmHg. The *tosylhydrazone* of (*E*)-1-acetyl-2-(2-methylethenyl)benzene was prepared by heating the (*E*)-ketone with an equimolar amount of toluene-*p*-sulphonohydrazide in ethanol under reflux for 1.5 h; cooling gave crystals (76%), m.p. 159—162 °C (from ethanol) (Found: C, 66.0; H, 6.0; N, 8.6. $C_{18}H_{20}N_2O_2S$ requires C, 65.8; H, 6.1; N, 8.5%); $\nu_{max.}$(Nujol) 3 220 cm^{-1} (NH). A similar reaction of the *E*/*Z* isomer mixture of 1-acetyl-2-(2-methylethenyl)benzene followed by chromatography of the product (silica, 50 vol % ether in light petroleum) gave (a) (Z)-1-*acetyl*-2-(2-*methylethenyl*)*benzene tosylhydrazone* (35%), m.p. 127—130 °C (from ethanol) (Found: C, 65.9; H, 6.2; N, 8.5. $C_{18}H_{20}N_2O_2S$ requires C, 65.8; H, 6.1; N, 8.5%); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH); δ_H (100 MHz) 1.77 (3 H, dd, *J* 7 and 1.5 Hz), 2.10 (3 H, s, MeC=N), 2.43 (3 H, s, tosyl Me), 5.58 (1 H, dq, *J* 12 and 7 Hz, 2'-H), 5.85 (1 H, dq, *J* 12 and 1.5 Hz), and 6.80—7.79 (9 H, m, NH and aromatic); and (b) the isomeric (*E*)-tosylhydrazone (24%), m.p. 159—162 °C, identical with that prepared above.

(v) 1-*Formyl*-2-(2,2-*dimethylethenyl*)*benzene*. A Wittig reaction of 2-bromobenzyltriphenylphosphonium bromide (100 g, 0.195 mol) and acetone (11.8 g, 0.2 mol) using the method above gave after chromatography an oil which was distilled to give 1-bromo-2-(2,2-dimethylethenyl)benzene (27.9 g, 68%), b.p. 52 °C at 0.4 mmHg (Found: *m/z* 212.001 119. $C_{10}H_{11}{}^{81}Br$ requires M^+ 212.002 491); δ_H (100 MHz) 1.68 (3 H, d, *J* 1.5 Hz, *Z*-Me), 1.86 (3 H, d, *J* 1.5 Hz, *E*-Me), 6.20 (1 H, m, 1'-H), 6.88—7.20 (3 H, m, aromatic), and 7.48 (1 H, m, aromatic). A Grignard reagent prepared from this halide (27.9 g, 0.132 mol) and magnesium (3.4 g, 0.14 g-atom) in ether (100 ml) on reaction with dimethylformamide (13.5 g, 0.17 mol) as described above gave a yellow oil (18.1 g) which on distillation gave 1-formyl-2-(2,2-dimethylethenyl)benzene (15.9 g, 75%), b.p. 64 °C at 1.0 mmHg (Found: C, 82.3; H, 7.5. $C_{11}H_{12}O$ requires C, 82.5; H, 7.5%); δ_H (100 MHz) 1.61 (3 H, d, *J* 1.5 Hz, *Z*-Me), 1.91 (3 H, d, *J* 1.5 Hz, *E*-Me), 6.52 (1 H, br s, 1'-H), 7.16—7.58 (3 H, m, aromatic), 7.85 (1 H, m, aromatic), and 10.20 (1 H, s, CHO). *Tosylhydrazone* (81%), m.p. 110—112 °C (from ethanol) (Found: C, 65.7; H, 6.2; N, 8.5. $C_{18}H_{20}N_2O_2S$ requires C, 65.8; H, 6.1; N, 8.5%); $\nu_{max.}$(Nujol) 3 240 cm^{-1} (NH).

(vi) 1-*Formyl*-2-(2,2-*diphenylethenyl*)*benzene*. A solution of potassium t-butoxide (6.6 g, 0.059 mol) in t-butyl alcohol (100 ml) was added during 2 h to a stirred refluxing mixture of 2-bromobenzyltriphenylphosphonium bromide (30 g, 0.058 mol) and benzophenone (10.9 g, 0.058 mol) in t-butyl alcohol (100 ml). The reaction mixture was heated under reflux for 15 h and then evaporated to low volume under reduced pressure. Extraction with dichloromethane, water washing, drying, and evaporation of the solvent gave an oil (14.7 g). Chromatography (alumina, light petroleum) gave 1-bromo-2-(2,2-diphenylethenyl)benzene (12.0 g, 61%), m.p. 61.5—62.5 °C (from ethanol) (lit.,[34] 61.5—62.5 °C). A Grignard reagent from this halide (11.8 g, 0.035 mol) and magnesium (1.0 g, 0.04 g-atom) in ether (70 ml) on reaction with dimethylformamide (5.0 g, 0.065 mol) as described above gave an oil (8.1 g) which was crystallised to give 1-*formyl*-2-(2,2-*diphenylethenyl*)*benzene* (7.1 g, 70%), m.p. 102—103 °C (from ethanol) (Found: *m/z* 284.119 060. $C_{21}H_{16}O$ requires M^+ 284.120 109), δ_H (100 MHz) 6.92—7.75 (15 H, aromatic and olefinic) and 10.21 (1 H, s, CHO); $\nu_{max.}$(Nujol) 1 690 cm^{-1} (C=O). *Tosylhydrazone* (79%), m.p. 167—168 °C (from ethanol) (Found: C, 74.2; H, 5.4; N, 6.1. $C_{28}H_{24}N_2O_2S$ requires C, 74.3; H, 5.4; N, 6.2%); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH).

(vii) (E)-2-(2-*Ethoxycarbonylethenyl*)*benzaldehyde*. Diethyl ethoxycarbonylmethylphosphonate (9.8 g, 0.05 mol) was added during 5 min to a stirred solution of sodium ethoxide [(0.052 mol) from sodium (1.2 g)] in ethanol (100 ml) at room temperature. 1-Formyl-2-benzaldehyde ethylene acetal (8.90 g, 0.05 mol) was added, and the mixture was stirred at room temperature for 5 min and then diluted with water (500 ml). Extraction with ether (3 × 100 ml), drying, and evaporation of the solvent gave a yellow oil (11.9 g). Chromatography (silica, 50 vol % ether in light petroleum) gave (E)-2-(2-*ethoxycarbonylethenyl*)*benzaldehyde ethylene acetal* (9.3 g, 75%), b.p. 135 °C at 0.1 mmHg (Found: C, 68.0; H, 6.6. $C_{14}H_{16}O_4$ requires C, 67.7; H, 6.5%); δ_H (100 MHz) 1.28 (3 H, t, *J* 7 Hz, Me), 3.85—4.12 (4 H, m, CH_2CH_2), 4.24 (2 H, q, *J* 7 Hz, CH_2), 5.95 (1 H, s, acetal CH), 6.32 (1 H, d, *J* 16 Hz, 1'-H), 7.32—7.65 (4 H, m, aromatic), and 8.18 (1 H, d, *J* 16 Hz, 2'-H); $\nu_{max.}$(film) 1 710 cm^{-1} (C=O). This compound (8.0 g) was shaken with hydrochloric acid (100 ml; 3M) for 24 h. Extraction with dichloromethane, washing with water (2 × 100 ml), drying, and evaporation gave a yellow oil (6.4 g) which on distillation gave (E)-2-(2-*ethoxycarbonylethenyl*)*benzaldehyde* (5.4 g, 83%), b.p. 120 °C at 0.1 mmHg (Found: C, 70.7; H, 6.0. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%); δ_H (100 MHz) 1.31 (3 H, t, *J* 7 Hz, Me), 4.24 (2 H, q, *J* 7 Hz, CH_2), 6.32 (1 H, d, *J* 16 Hz, 1'-H), 7.29—7.70 (3 H, m, aromatic), 7.83 (1 H, m, aromatic), 8.49 (1 H, d, *J* 16 Hz, 2'-H), and 10.24 (1 H, s, CHO); $\nu_{max.}$(film) 1 710 (ester C=O), 1 640 cm^{-1} (aldehyde C=O). Tosylhydrazone (71%), m.p. 117—118 °C (from ethanol) (Found: C, 61.1; H, 5.4; N, 7.5. $C_{19}H_{20}N_2O_4S$ requires C, 61.3; H, 5.4; N, 7.5%); $\nu_{max.}$(Nujol) 3 190 cm^{-1} (NH).

(viii) (E)-2-(2-*Ethoxycarbonylethenyl*)-3-*formylthiophene*. The reaction between diethylethoxycarbonylmethylphosphonate (4.9 g, 0.025 mol) and 2-formyl-3-thienylaldehyde ethylene acetal (4.0 g, 0.025 mol) as described above gave a yellow solid (5.39 g) which was crystallised to give (E)-2-(2-*ethoxycarbonylethenyl*)-*thiophene*-3-*carbaldehyde ethylene acetal* (4.8 g, 87%), m.p. 52—53 °C (from ethanol) (Found: C, 56.8; H, 5.6. $C_{12}H_{14}O_4S$ requires C, 56.7; H, 5.6%); δ_H (100 MHz) 1.32 (3 H, t, *J* 7 Hz, Me), 4.04 (4 H, br s, CH_2CH_2), 4.20 (2 H, q, *J* 7 Hz, CH_2), 5.97 (1 H, s, acetal CH), 6.24 (1 H, d, *J* 16 Hz, 1'-H), 7.12 (1 H, d, *J* 5 Hz, 4-H), 7.31 (1 H, d, *J* 5 Hz, 5-H), and 7.98 (1 H, d, *J* 16 Hz, 2'-H); $\nu_{max.}$(Nujol) 1 705 cm^{-1} (C=O). This compound (4.4 g) was dissolved in dichloromethane (10 ml) and shaken with hydrochloric acid (100 ml; 3M) for 30 min. Extraction with dichloromethane (50 ml), washing with water, drying, and evaporation gave a green oil (3.52 g). Distillation gave a colourless oil (3.1 g), b.p. 140 °C at 0.1 mmHg which solidified and was crystallised to give (E)-2-(2-*ethoxycarbonylethenyl*)-3-*formylthiophene* (2.72 g, 75%), m.p. 37—38 °C (from ethanol) (Found: C, 57.2; H, 4.8. $C_{10}H_{10}O_3S$ requires C, 57.1; H, 4.8%); δ_H (100 MHz) 1.30 (3 H, t, *J* 7 Hz, Me), 4.24 (2 H, q, *J* 7 Hz, CH_2), 6.36 (1 H, d, *J* 16 Hz, 1'-H), 7.30 (1 H, d, *J* 5 Hz, 4-H), 7.44 (1 H, d, *J* 5 Hz, 5-H), 8.32 (1 H, d, *J* 16 Hz, 2'-H), and 10.18 (1 H, s, CHO); $\nu_{max.}$(Nujol) 1 720 (ester C=O), 1 688 cm^{-1} (aldehyde C=O). The usual method of preparing the tosylhydrazone gave no crystals. Evaporation left a red oil (4.25 g) which on chromatography (silica, 75 vol % ether in light petroleum) gave the *tosylhydrazone* as colourless crystals (2.4 g, 60%), m.p. 138—139 °C (from ethanol) (Found: C, 53.9; H, 4.8; N, 7.4. $C_{17}H_{18}N_2O_4S_2$ requires C, 54.0; H, 4.8; N, 7.4%); $\nu_{max.}$(Nujol) 3 160 cm^{-1} (NH).

(ix) (E)-2-(2-*Ethoxycarbonyl*-2-*methylethenyl*)-3-*formylthiophene*. The reaction between diethyl 1-ethoxycarbonylethylphosphonate (13.0 g, 0.052 mol) and 2-formyl-thiophene-3-carbaldehyde ethylene acetal (8.0 g, 0.052 mol) as described above gave a yellow oil which on distillation gave (E)-2-(2-*ethoxycarbonyl*-2-*methylethenyl*)*thiophene*-3-*carbaldehyde ethylene acetal* (1.11 g, 76%), b.p. 170 °C at 0.8 mmHg (Found: *m/z* 268.075 996. $C_{13}H_{16}O_4S$ requires M^+ 268.076 924); δ_H (100 MHz) 1.31 (3 H, t, *J* 7 Hz, ester Me), 2.19 (2 H, d, *J* 2 Hz, 2'-Me), 3.95—4.18 (4 H, m, acetal CH_2CH_2), 4.24 (2 H, q, *J* 7 Hz, CH_2), 6.01 (1 H, s, acetal CH), 7.18 (1 H, d, *J* 5 Hz, 4-H), 7.37 (1 H, d, *J* 5 Hz), and 8.09 (1 H, q, *J* 2 Hz, 1'-H); $\nu_{max.}$(film) 1 705 cm^{-1} (C=O). This compound (1.80 g) was shaken with hydrochloric acid (20 ml; 3M) for 30 min. The usual work-up followed by distillation gave (E)-2-(2-*ethoxycarbonyl*-2-*methylethenyl*)-3-*formylthiophene* as a yellow oil (1.30 g, 86%), b.p. 150 °C at 0.3 mmHg (Found: *m/z* 224.050 976. $C_{11}H_{12}O_3S$ requires M^+ 224.050 711); δ_H (100 MHz) 1.34 (3 H, t, *J* 7 Hz, ester Me), 2.19 (3 H, d, *J* 2 Hz, 2'-Me), 4.25 (2 H, q, *J* 7 Hz, ester CH_2), 7.38 (1 H, d, *J* 5 Hz, 4-H), 7.50 (1 H, d, *J* 5 Hz, 5-H), 8.41 (1 H, m, *J* 2 Hz, 1'-H), and 10.19 (1 H, s, CHO); $\nu_{max.}$(Nujol) 1 685 cm^{-1} (C=O). *Tosylhydrazone* (63%), m.p. 147—148 °C (from ethanol) (Found: C, 55.1; H, 5.1; N, 7.1. $C_{18}H_{20}N_2O_4S_2$ requires C, 55.1; H, 5.1; N, 7.1%); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH).

Decomposition of the Sodium Salts of the Tosylhydrazones.—The sodium salts were prepared and dried as described previously[2] and decomposed at reflux temperature, under nitrogen, in the solvent indicated. When the reaction was complete (as shown by t.l.c. monitoring) the reaction mixture was cooled, added to water, and extracted with ether. The organic layer was separated, dried, and evaporated to give the crude product or mixture.

(E)-1-*Formyl*-2-(2-*phenylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (8.0 g, 0.0210 mol) salt in DME (200 ml) was boiled under reflux for 15 min. The usual work-up gave a yellow oil which by chromatography (silica, 5 vol % ether in light petroleum) gave 4-phenyl-1*H*-2,3-benzodiazepine (**34b**) (4.0 g, 85%), m.p. 131—132 °C (from ethanol) (lit.,[2] 132—133 °C). A similar reaction in cyclohexane gave the same product (83%).

(Z)-1-*Formyl*-2-(2-*phenylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (4.0 g, 0.011 mol) salt in cyclohexane (200 ml) was boiled under reflux for 8 h. Chromatography (silica, 5 vol % ether in light petroleum) gave: (a) (Z)-1-*cyclohexylmethyl*-2-*phenylethenyl*)*benzene* (0.31 g, 10%), b.p. 200 °C at 0.2 mmHg (Found: *m/z* 276.186 736. $C_{21}H_{24}$ requires M^+ 276.187 792); δ_H (100 MHz) 0.65—1.83 (11 H, m, cyclohexyl), 2.52 (2 H, d, *J* 6 Hz, CH_2Ar), 6.52 (1 H, d, *J* 11 Hz, ArCH=), 6.68 (1 H, d, *J* 11 Hz, =CHPh), and 6.85—7.22 (9 H, m, aromatic); *m/z* 276 (100), 193 (53), 185 (56), 179 (25), 143 (18), 129 (19), 117 (59), 115 (50), and 91 (31%); (b) 9H-*cyclohepta*[a]*naphthalene* (0.86 g, 42%), m.p. 98—99 °C (from ethanol) (Found: C, 93.6; H, 6.2. $C_{15}H_{12}$ requires C, 93.7; H, 6.3%); δ_H (100 MHz) 2.30 (2 H, t, *J* 7 Hz, 9-H_2), 5.84 (1 H, dt, *J* 10 and 7 Hz, 8-H), 5.95 (1 H, dt, *J* 10 and 7 Hz, 10-H), 6.75 (1 H, d, *J* 10 Hz, 7-H), 7.12 (1 H, d, *J* 10 Hz, 11-H), and 7.31—8.20 (6 H, m, aromatic); δ_C (20 MHz) 26.3 (C-9), 124.6, 125.0, 125.6, 126.0, 126.4, 126.6, 128.1, 128.6, 130.2 131.6 (tert.), 132.0 (tert.), 133.4 (tert.), and 134.7 p.p.m. (tert.); *m/z* 192 (M^+, 100%); and (c) (Z)-1-*formyl*-2-*phenylethenyl*)*benzene azine* (0.61 g, 28%), as yellow crystals, m.p. 138—139 °C (from ethanol) (Found: C, 87.6; H, 5.9; N, 6.7. $C_{30}H_{24}N_2$ requires C, 87.4; H, 5.9; N, 6.8%); δ_D (100 MHz) 6.69 (1 H, d, *J* 12 Hz, =CHPh), 6.82 (1 H, d, *J* 12 Hz, ArCH=), 7.03—8.18 (9 H, m, aromatic), and 8.78 (1 H, s, CH=N); *m/z* 412 (62), 345 (55), 282 (20), 206 (100), 191 (40), 178 (30), 130 (50), and 128 (28%); $\nu_{max.}$(Nujol) 1 610 cm^{-1} (C=N).

1-*Formyl*-2-(2,2-*diphenylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (3.0 g, 0.0066 mol) in cyclohexane (150 ml) was boiled under reflux for 45 h. Chromatography (silica, 50 vol % ether in light petroleum) gave: (a) 6-*phenyl*-9H-*cyclohepta*[a]-*naphthalene* (**21**) (0.84 g, 47%), m.p. 98—99 °C (from ethanol) (Found: C, 94.0; H, 6.1. $C_{21}H_{16}$ requires C, 94.0; H, 6.0%); δ_H (360 MHz) 2.32 (2 H, t, *J* 7 Hz, 9-H_2), 5.80 (1 H, dt, *J* 10 and 7 Hz, 8-H), 6.04 (1 H, dt, *J* 10 and 7 Hz, 10-H), 6.39 (1 H, d, *J* 10 Hz, 7-H), 7.17 (1 H, d, *J* 10 Hz, 11-H), 7.28—7.53 (7 H, m, aromatic), 7.62 (1 H, s, 5-H), 7.75 (1 H, br d, *J* 8.5 Hz, aromatic), and 8.14 (1 H, br d, *J* 8.5 Hz, aromatic); δ_C 26.6 (C-9), 124.8, 125.0, 126.0, 126.1, 127.0, 127.3 (tert.), 127.5, 127.9, 128.0, 128.2, 128.9, 129.9, 131.5, 133.8 (tert.), 133.9 (tert.), 140.3 (tert.), and 141.8 (tert.); *m/z* 268 (M^+, 100%) and (b) (Z)-1-*formyl*-2-(2,2-*diphenylethenyl*)*benzene azine* 0.54 g, 29%), as yellow crystals, m.p. 188—190 °C (from carbon tetrachloride) (Found: C, 89.1; H, 5.6; N, 4.8. $C_{42}H_{32}N_2$ requires C, 89.3; H, 5.7; N, 5.0%); δ_H (100 MHz) 6.80—7.40 (1 H, m, aromatic and olefinic), 7.92 (1 H, m, aromatic), and 8.98 (1 H, s, CH=N); *m/z* 564 (77), 487 (32), 282 (100), 207 (57), 205 (42), 181 (28), and 169 (45%).

(Z)-1-*Formyl*-2-(2-*methyl*-2-*phenylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (2.0 g, 0.0051 mol) salt in cyclohexane (100 ml) was boiled under reflux for 15 h. Chromatography (silica, 5 vol % ether in light petroleum) gave: (a) 6-*methyl*-9H-*cyclohepta*[a]*naphthalene* (0.81 g, 76%), as an oil, b.p. 200 °C at 0.3 mmHg (Found: C, 93.0; H, 7.0. $C_{16}H_{14}$ requires C, 93.2; H, 6.8%); δ_H (100 MHz) 2.25 (2 H, t, *J* 7 Hz, 9-H_2), 2.45 (3 H, s, Me), 6.0 (2 H, dt, *J* 10 and 7 Hz, 8- and 10-H), 6.71 (1 H, d, *J* 10 Hz, 7-H), 7.16 (1 H, d, *J* 10 Hz, 11-H), and 7.10—8.20 (5 H, m, aromatic); δ_C 21.4 (Me), 26.5 (C-9), 124.6, 125.0, 125.3, 125.6, 125.8, 126.5, 126.6, 127.8, 128.3, 129.8 (tert.), 130.3 (tert.), 134.3 (tert.), and 136.9 (tert.); *m/z 206* [M^+, 100%); and (b) (Z)-1-*formyl*-2-(2-*methyl*-2-*phenylethenyl*)*benzene azine* (0.12 g, 11%), as yellow crystals, m.p. 211—213 °C (from ethyl acetate) (Found: C, 87.1; H, 6.4; N, 6.3. $C_{32}H_{28}N_2$ requires C, 87.2; H, 6.4; N, 6.4%; δ_H (100 MHz) 2.26 (3 H, d, *J* 1.5 Hz, Me), 6.72 (1 H, q, *J* 1.5 Hz, olefinic), 6.82—7.25 (8 H, m, aromatic), 8.00 (1 H, m, aromatic), and 8.85 (1 H, s, CH=N); *m/z* 440 (2), 428 (15), 307 (50), 220 (100), 207 (73), 178 (59), and 105 (60%).

(E)-1-*Formyl*-2-(2-*methyl*-2-*phenylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (1.0 g, 0.0025 mol) salt in cyclohexane (50 ml) was heated under reflux for 7 h. Chromatography (silica, 50 vol % ether in light petroleum) gave (E)-1-*formyl*-2-(2-*methyl*-2-*phenylethenyl*)*benzene azine* (0.45 g, 81%), as yellow crystals, m.p. 173—174 °C (from ethyl acetate) (Found: C, 87.3; H, 6.4; N, 6.3. $C_{32}H_{28}N_2$ requires C, 87.2; H, 6.4; N, 6.4%); δ_H (100 MHz) 2.10 (3 H, d, *J* 1.5 Hz, Me), 7.05 (1 H, q, *J* 1.5 Hz, olefinic), 7.20—7.60 (8 H, m, aromatic). 8.14 (1 H, m, aromatic), and 8.85 (1 H, s, CH=N); *m/z* 440 (50), 425 (70), 363 (55), 220 (100), 206 (65), 144 (25), and 115 (27%).

(E)-1-*Formyl*-2-(2-*methylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (4.0 g, 0.012 mol) salt in cyclohexane (200 ml) was boiled under reflux for 1 h. Chromatography (silica, 50 vol % ether in light petroleum) gave 4-*methyl*-1H-2,3-*benzodiazepine* (**34a**) (1.51 g, 76%), m.p. 66—67 °C (from ethanol) (Found: C, 75.9; H, 6.4; N, 17.8. $C_{10}H_{10}N_2$ requires C, 75.9; H, 6.4; N, 17.7%); δ_H (100 MHz) 2.45 (3 H, d, *J* 1.5 Hz, 4-Me), 2.87 (1 H, d, *J* 10 Hz, 1-H_{ax}), 6.21 (1 H, d, *J* 10 Hz, 1-H_{eq}), 6.41 (1 H, q, *J* 1.5 Hz, 5-H), and 7.18—7.46 (4 H, m, aromatic); T_C 77 ± 10 °C; δ_C (20 MHz) 21.2 (Me), 68.7 (C-1), 115.9 (C-5), 150.2 (C-4), 125.4 (tert.), 127.0, 127.4, 128.0, 130.0 (tert.), and 133.6 p.p.m. (tert.).

(Z)-1-*Formyl*-2-(2-*methylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (4.31 g, 0.0135 mol) in cyclohexane (200 ml) was boiled under reflux for 10 h. Chromatography (silica, 5 vol % ether in light petroleum) gave: (a) (Z)-1-*cyclohexylmethyl*-2-(2-*methylethenyl*)*benzene* (0.44 g, 15%), as an oil, b.p. 80 °C at 0.2 mmHg (Found: *m/z* 214.172 025. $C_{16}H_{22}$ requires M^+ 214.172 142); δ_H (100 MHz) 0.81—1.80 (11 H, m, cyclohexyl), 1.70 (3 H, dd, *J* 7 and 1.5 Hz, Me), 2.45 (2 H, d, *J* 6 Hz, CH_2Ar),

5.81 (1 H, dq, *J* 10 and 7 Hz, =C*H*Me), 6.50 (1 H, dq, *J* 10 and 1.5 Hz, ArCH=), and 7.08 (4 H, s, aromatic); *m/z* 214 (34), 185 (100), 131 (60), 130 (68), 129 (66), 117 (69), 115 (54), and 91 (40%); and (b) (Z)-1-*formyl*-2-(2-*methylethenyl*)*benzene azine* (0.96 g, 49%), as a yellow oil, b.p. 240 °C at 0.2 mmHg (Found: *m/z* 288.161 995. $C_{20}H_{20}N_2$ requires M^+ 288.162 641); $\nu_{max.}$(film) 1 610 cm^{-1} (C=N); δ_H (100 MHz) 1.65 (3 H, dd, *J* 7 and 1.5 Hz, Me), 5.88 (1 H, dq, *J* 10 and 7 Hz, =CHMe), 6.78 (1 H, dq, *J* 10 and 1.5 Hz, ArCH=), 7.15—7.45 (3 H, m, aromatic), 8.15 (1 H, m, aromatic), and 8.85 (1 H, s, CH=N); *m/z* 288 (11), 273 (96), 144 (88), 130 (100), and 115 (37%).

1-*Formyl*-2-(2,2-*dimethylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (3.0 g, 0.0091 mol) salt in cyclohexane (150 ml) was boiled under reflux for 30 h. Chromatography (silica, graded elution 0—50 vol % ether in light petroleum) gave: (a) 1-*cyclohexylmethyl*-2-(2,2-*dimethylethenyl*)*benzene* (0.21 g, 11%), as an oil, b.p. 85 °C at 0.2 mmHg (Found: C, 89.1; H, 10.8. $C_{17}H_{24}$ requires C, 89.4; H, 10.6%); δ_H (100 MHz) 0.65—1.85 (11 H, m, cyclohexyl), 1.68 (3 H, d, *J* 1.5 Hz, *Z*-Me), 1.90 (3 H, d, *J* 1.5 Hz, *E*-Me), 2.45 (2 H, d, *J* 6 Hz, ArC*H*$_2$), 6.40 (1 H, m, ArCH=), and 7.11 (4 H, s, aromatic); *m/z* 228 (1), 188 (3), 170 (10), 156 (15), 146 (10), 119 (17), 85 (34), 71 (55), 57 (100), and 43 (60%); (b) (E)-1,2-*bis*[2-(2,2-*dimethylethenyl*)*phenyl*]*ethene* (0.43 g, 40%) m.p. 52—54 °C (from ethanol) (Found: C, 91.7; H, 8.6. $C_{22}H_{24}$ requires C, 91.6; H, 8.4%); δ_H (100 MHz) 1.65 (3 H, d, *J* 1.5 Hz, *Z*-Me), 1.89 (3 H, d, *J* 1.5 Hz, *E*-Me), 6.35 (1 H, m, olefinic), 7.05—7.30 (4 H, m, aromatic and olefinic), and 7.55 (1 H, m, aromatic); *m/z* 288 (M^+, 100%); and (c) 1-*formyl*-2-(2,2-*dimethylethenyl*)*benzene azine* (0.52 g, 38%), as yellow crystals, m.p. 122—123 °C (from ethanol) (Found: C, 83.8; H, 7.7; N, 8.7. $C_{22}H_{24}N_2$ requires C, 83.5; H, 7.6; N, 8.8%); $\nu_{max.}$(Nujol) 1 625 cm^{-1} (C=N); δ_H (100 MHz) 1.62 (3 H, d, *J* 1.5 Hz, *Z*-Me), 1.96 (3 H, d, *J* 1.5 Hz, *E*-Me), 6.41 (1 H, m, olefinic), 7.09—7.45 (3 H, m, aromatic), 8.16 (1 H, m, aromatic), and 8.92 (1 H, s, CH=N); *m/z* 316 (29), 301 (100), 158 (90), 144 (68), 129 (16), 116 (19), 115 (19), and 91 (16%).

1-*Acetyl*-2-(2-*methylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (3.0 g, 0.0091 mol) salt in cyclohexane (150 ml) was boiled under reflux for 4 h. Chromatography (silica, 50 vol % ether in light petroleum) gave 1,4-*dimethyl*-1H-2,3-*benzodiazepine* (**39**) (1.40 g, 89%), as a yellow oil (Found: C, 76.9; H, 7.1; N, 16.4. $C_{11}H_{12}N_2$ requires C, 76.7; H, 7.0; N, 16.3%); δ_H (100 MHz) 2.25 (3 H, d, *J* 6 Hz, 1-Me), 2.50 (3 H, d, *J* 1.5 Hz, 4-Me), 2.79 (1 H, q, *J* 6 Hz, 1-H), 6.50 (1 H, q, *J* 1.5 Hz, 5-H), and 7.22—7.61 (4 H, m, aromatic); δ_C (20 MHz) 20.8 (1-Me), 21.0 (4-Me), 70.6 (C-1), 115.7 (C-5), 150.0 (C-4), 115.8, 123.6, 126.9, 127.3, 128.9, 130.2 (tert.), and 133.3 p.p.m. (tert.).

(Z)-1-*Acetyl*-2-(2-*methylethenyl*)*benzene tosylhydrazone*. The tosylhydrazone (1.9 g, 0.0058 mol) salt in cyclohexane (100 ml) was boiled under reflux for 7 h. The usual work-up gave an oil which by g.l.c. analysis (3% OVI; 114 °C) contained one major component with three minor (< 10%) ones. Distillation gave a mixture containing predominantly 2,3-dimethylindene (**37**) (0.80 g, 80%), b.p. 85 °C at 0.2 mmHg (lit.,[35] 130 °C at 30 mmHg) (Found: *m/z* 114.093 925. Calc. for $C_{11}H_{12}$: M^+ requires 114.093 396); δ_H (100 MHz) 2.05 (6 H, s, 2 × Me), 3.20 (2 H, br s, CH_2), and 6.95—7.38 (4 H, m, aromatic).

(E)-2-(2-*Ethoxycarbonylethenyl*)-3-*formylthiophene tosylhydrazone*. The tosylhydrazone (1.8 g, 0.0047 mol) salt in DME (90 ml) was boiled under reflux for 30 min. The reaction mixture was filtered through Celite and the solvent was evaporated to leave a black oil. Chromatography (silica, 50 vol % ether in light petroleum) gave 4-*ethoxycarbonyl*-1H-*thieno*[3,2-d][1,2]*diazepine* (**23**) (0.81 g, 76%), as yellow crystals, m.p. 103—104 °C (from ethanol) (Found: *m/z* 222.047 024. $C_{10}H_{10}N_2O_2S$ requires M^+ 222.046 295); δ_H (100 MHz) (−28 °C) 1.41 (3 H, t, *J* 7 Hz, Me), 2.53 (1 H, d, *J* 10 Hz, 1-H_{ax}), 4.46 (2 H, q, *J* 7 Hz, ester CH_2), 6.75 (1 H, d, *J* 10 Hz, 1-H_{eq}), 7.11 (1 H, d, *J* 5 Hz, 8-H), 7.63 (1 H, s, 5-H), and 7.78 (1 H, d, *J* 5 Hz, 7-H); T_C 65 ± 10 °C (for peaks δ 2.53 and 6.75).

(E)-2-(2-*Ethoxycarbonyl*-2-*methylethenyl*)-3-*formylthiophene tosylhydrazone*. (i) *In DME*. The tosylhydrazone (1.1 g, 0.0028 mol) salt in DME (50 ml) was heated under reflux for 45 min. Chromatography gave: (a) (E)- or (Z)-1,2-*bis*{2-[(E)-2-*ethoxycarbonyl*-2-*methylethenyl*]-3-*thienyl*}*ethene* (0.0868 g, 15%), m.p. 81—82 °C (from ethanol) (Found: *m/z* 416.112 128. $C_{22}H_{24}O_4S_2$ requires M^+ 416.111 593); δ_H (100 MHz) 1.25 (3 H, t, *J* 7 Hz, ester Me), 2.12 (3 H, d, *J* 1.5 Hz, Me), 4.20 (2 H, q, *J* 7 Hz, ester CH_2), 6.70—7.44 (3 H, m, thienyl and olefinic), and 7.84 (1 H, m, CH=CMeCO_2Et); $\nu_{max.}$(Nujol) 1 695 (C=O), and 1 610 cm^{-1} (C=C); *m/z* 416 (88), 297 (100), 269 (39), 254 (27), 241 (36), 147 (15), and 135 (27%); and (b) the other geometric isomer (0.0683 g, 12%), m.p. 150—153 °C (from methanol) (Found: *m/z* 416.112 942. $C_{22}H_{24}O_4S_2$ requires M^+ 416.111 593); δ_H (100 MHz) 1.31 (3 H, t, *J* 7 Hz, ester Me), 2.20 (3 H, d, *J* 1.5 Hz, Me), 4.30 (2 H, q, *J* 7 Hz, ester CH_2), and 6.25—7.21 (4 H, m, thienyl); $\nu_{max.}$(Nujol) 1 698 (C=O), 1 605 cm^{-1} (C=C); *m/z* 416 (78), 401 (39), 297 (100), 269 (43), 254 (28), 241 (35), 150 (35), and 145 (30%).

(ii) *In cyclohexene*. The tosylhydrazone (3.3 g, 0.0084 mol) salt in cyclohexene (150 ml) was boiled under reflux for 3.5 h. Chromatography (silica, 10 vol % ether in light petroleum) gave an isomeric mixture which contained predominantly (E)-3-*bicyclo*[4.1.0]*heptan*-7-*yl*-2-(2-*ethoxycarbonyl*-2-*methylethenyl*)-*thiophene* (1.51 g, 62%), as a mixture of *exo*- and *endo*-isomers, b.p. 110 °C at 0.5 mmHg (Found: C, 70.5; H, 7.6. $C_{17}H_{22}O_2S$ requires C, 70.3; H, 7.6%); δ_H (100 MHz) 0.9—2.5 (10 H, m, cyclohexyl), 1.30 (3 H, t, *J*, 7 Hz, ester Me), 2.20 (3 H, d, *J* 1.5 Hz, Me), 4.24 (2 H, q, *J* 7 Hz, ester CH_2), 6.55—7.42 (2 H, m, thiophene), and 7.94 and 8.14 (1 H, br s, CH=, *exo* and *endo*); $\nu_{max.}$(film) 1 700 cm^{-1} (C=O); *m/z* 290 (72), 217 (28), 209 (19), 193 (36), 189 (25), 161 (22), 149 (36), 147 (28), 135 (47), 97 (25), 81 (100), and 80 (42%).

(E)-2-(2-*Ethoxycarbonylethenyl*)*benzaldehyde tosylhydrazone*. This tosylhydrazone salt on heating in DME for 1 h gave a dark yellow oil shown by t.l.c. (silica, 50 vol % ether in light petroleum) to contain more than 20 components. Separation was not attempted.

* *Note added in proof*. We therefore conclude that the experimental results obtained so far on the cyclisations of α,-β:γ,δ- unsaturated diazo compounds can be best rationalised in terms of a primary 1,7-electrocyclisation step as dicussed above and elsewhere.[6] However, the reactions of such compounds at low temperatures, where such species as (50) might be stable, have yet to be studied.

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