# Formation of Di-iron Hexacarbonyl Complexes of 3*H*-1,2-Diazepines and the Effects of Complexation on Ring Inversion and the Rate of Sigmatropic Hydrogen Migration

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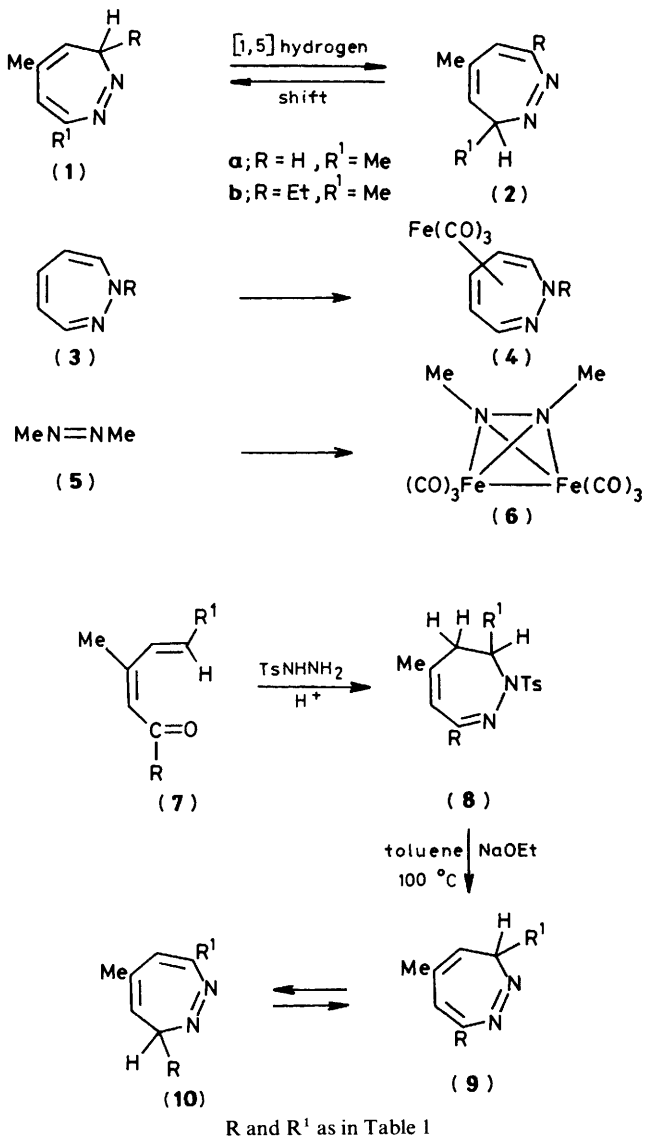
A number of 3*H*-1,2-diazepines [(**9**)/(**10**) (**a**—**f**)] have been synthesised by the reactions of 6,7-dihydro-1-tosyl-1,2-diazepines with base. These diazepines are in dynamic equilibrium at room temperature *via* [1,5] sigmatropic hydrogen migrations but in some cases could be separated by h.p.l.c. at 0 °C. The reactions of 1*H*-2,3-benzodiazepines, 3*H*-1,2-benzodiazepines and the monocylic 3*H*-1,2-diazepines (**9**)/(**10**) with di-iron nonacarbonyl gave the dinuclear iron hexacarbonyl complexes (**12**), (**14**), and (**15**)/(**16**), respectively, in moderate yield. The complexes were found to undergo ring inversion more easily than their precursors, and activation energies were determined. The complexation of the azo group also stopped the easy [1,5] sigmatropic hydrogen shift observed for (**9**)/(**10**) and this is discussed in terms of changes in electronic effect and in the structural geometry of the diazepine ring.

We have previously reported the synthesis of 3*H*-1,2-diazepines (**1**) and (**2**) by the base-induced elimination of toluene-*p*-sulphinic acid from 6,7-dihydro-1-tosyl-1,2-diazepines,[1]† and more recently by the cyclisation of unsaturated diazo compounds.[2] These diazepines were found to undergo rapid [1,5] sigmatropic hydrogen shifts at room temperature, interconverting (**1**) and (**2**) so that the individual isomers could not easily be isolated. Very small amounts of (**1a**) and (**2a**), and of (**1b**) and (**2b**), were isolated by high performance liquid chromatography at 0 °C and their return to equilibrium was monitored. Thus (**2a**) was found to have a half-life of *ca.* 30 min at 0 °C. The objectives of this work were to prepare metal complexes of the diazepines in the hope that the rate of the sigmatropic shifts would be diminished by complexation, so allowing the separation of the complexes of (**1**) and (**2**) and possibly the regeneration of the individual diazepines at low temperature by disengagement from the complexes.

Before the start of this work it was known that 1*H*-1,2-diazepines (**3**) form iron carbonyl complexes, *e.g.* (**4**), *via* co-ordination of the diene moiety,[3] and that azo compounds (**5**) form dinuclear iron carbonyl complexes, *e.g.* (**6**).[4] It was therefore of interest to discover how the 3*H*-1,2-diazepine system (which contains both a conjugated diene and an azo group) would react.

## Results and Discussion

(i) *Preparation of* 3H-1,2-*Diazepines* (**9**)/(**10**).—These compounds were prepared from the dienones (**7**) by the two-step route shown in Scheme 1.[1,5] The isomer ratios were determined from high resolution (360 MHz) $^1$H n.m.r. spectra of the mixtures and these data, together with similar results of earlier work, are shown in Table 1. Since the interconversion between the isomers is rapid at room temperature these ratios must reflect the relative thermodynamic stability of (**9**) and (**10**). This appears to be controlled largely by the conjugating capabilities of R and R$^1$. Thus in the two cases where R = phenyl, the only isomers detectable were (**9e**) and (**9f**) in which the phenyl group is conjugated with the diene system. Hyperconjugation to the methyl group stabilises (**9a**) relative to (**10a**) but this effect is apparently no greater than that of ethyl or phenethyl as shown



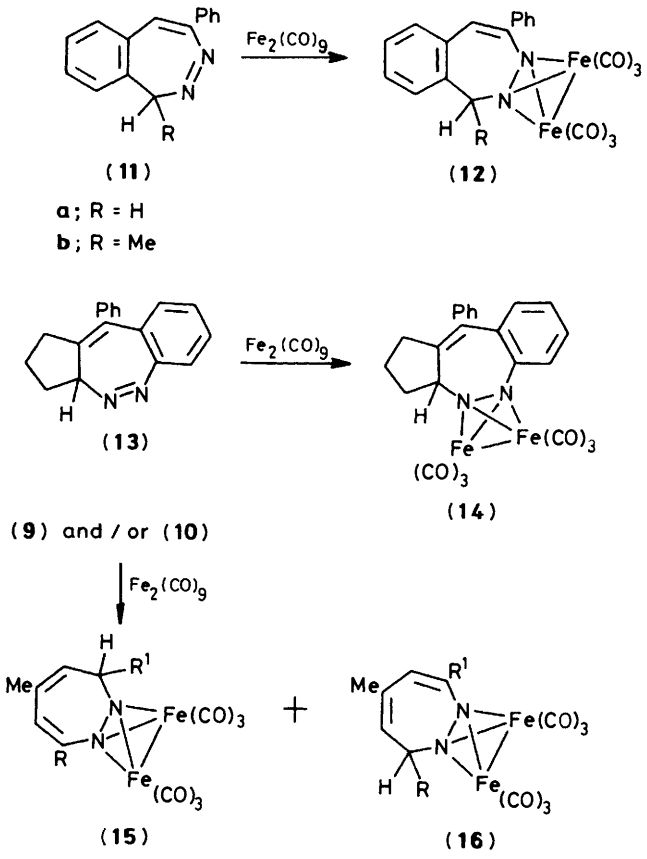

R and R$^1$ as in Table 1

**Scheme 1.**

† These compounds were numbered previously (ref. 1) as 3,4-dihydro-2-tosyl-1,2-diazepines.

**Table 1.** Yields and isomer ratios of 3*H*-1,2-diazepines (**9**) and (**10**)

| Precursor | R | $R^1$ | Total yield (%) | Ratio (**9**):(**10**) |
|---|---|---|---|---|
| (**8a**) | Me | H | 78 | 85:15 |
| (**8b**) | Et | Me | 88 | 52:48 |
| (**8c**) | $PhCH_2CH_2$ | Me | 93 | 51:49 |
| (**8d**) | $Pr^i$ | Me | 74 | 34:66 |
| (**8e**) | Ph | H | 82 | (**9e**) only |
| (**8f**) | Ph | Me | 84 | (**9f**) only |




**Scheme 2.**

by the *ca.* 1:1 ratios of (**9b**) to (**10b**) and (**9c**) to (**10c**). However conjugation of isopropyl is less effective and (**10d**) is the major component. In cases (**a**) and (**b**) it had been possible to separate the isomers by analytical scale h.p.l.c. at 0 °C,[1] but two of the new systems synthesised in this work, (**9c**)/(**10c**) and (**9d**)/(**10d**), were not separated either by adsorption h.p.l.c. on silica or by the reverse-phase technique using a bonded ODS stationary phase.

(ii) *Formation of Complexes.*—The initial experiments on complex formation were done with the benzo-annelated 3*H*-1,2-diazepine systems (**11**) and (**13**). Both the 1*H*-2,3-benzodiazepines (**11a** and **b**) and the 3*H*-1,2-benzodiazepine (**13**) reacted readily with di-iron nonacarbonyl in benzene at room temperature to give the dinuclear complexes (**12a** and **b**) and (**14**) in moderate yield (53—58%).

The monocyclic 3*H*-1,2-diazepines (**9**/**10a—e**) reacted in a similar way to give the complexes (**15**) and (**16**) (Scheme 2) in the yields and ratios shown in Table 2. The diazepines (**9a**)/(**10a**)

**Table 2.** Yields and isomer ratios of the dinuclear iron hexacarbonyl complexes (**15**) and (**16**) of 3*H*-1,2-diazepines

| Compounds | R | $R^1$ | Total yield (%) | Ratio (**15**):(**16**) |
|---|---|---|---|---|
| (**15a**) | Me | H | 31 (64[a]) | |
| (**15b**)/(**16b**) | Et | Me | 46 | 60:40 |
| (**15c**)/(**16c**) | $PhCH_2CH_2$ | Me | 38 | 72:28 |
| (**15d**)/(**16d**) | $Pr^i$ | Me | 57 | 88:12 |
| (**15e**) | Ph | H | 28 | |

[a] Benzylideneacetone iron tricarbonyl complex as reagent.

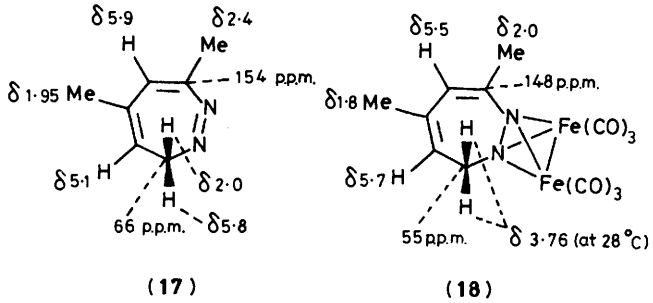
and (**9e**) gave single products, the isomer (**15**) in each case. This is not surprising for (**9e**) which was isomerically pure but more so for (**9a**)/(**10a**) which contains *ca.* 15% of (**10a**). The rather low yield of (**15a**) (31%) obtained in the reaction with di-iron nonacarbonyl was improved to 64% when benzylideneacetone iron tricarbonyl complex was used as the reagent, but in neither case could any of the isomer (**16a**) be detected by n.m.r. spectroscopy or by h.p.l.c. in the crude complex obtained after chromatography and before recrystallisation. It must be concluded that the major isomer (**9a**) reacts markedly faster with the complexing reagent than does (**10a**). The other monocyclic diazepines all gave mixtures of (**15**) and (**16**). It can be seen from the product ratios in Table 2 that the diazepine isomers (**9**/**10b—d**) also react at different rates so that the complex having the bulkier group (Et, $CH_2CH_2Ph$, and $Pr^i$, respectively) at the unsaturated site is formed in higher yield.

One of the objectives of this work was to convert the isomeric diazepines into derivatives which could be more easily separated. In the event it was found that complexation reduces the polarity of the molecule with the result that chromatographic separation is difficult: all the complexes are eluted rapidly on silica by light petroleum or hexane. Thus although the diazepine mixture (**9b**)/(**10b**) was separable by h.p.l.c. the derived mixture of complexes (**15b**)/(**16b**) was not. In the case of the isopropyl analogues (**9d**)/(**10d**) and (**15d**)/(**16d**) neither the diazepines or the complexes were separable. However the objective was realised with the phenethyl derivatives: although the diazepines themselves could not be separated, the complexes (**15c**) and (**16c**) were isolated on a small scale by chromatography on silica. As had been hoped, complexation dramatically reduced the rate of the sigmatropic hydrogen shift so that the isomers (**15c**) and (**16c**) did not interconvert even at 110 °C. Sigmatropic shifts in these systems are discussed further in section (iv).

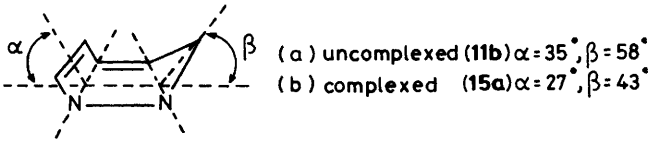
Not much work has yet been done on the disengagement of the diazepines from their dinuclear complexes. However reaction of the 1*H*-2,3-benzodiazepine complex (**12a**) with a large excess of trimethylamine oxide at room temperature gave the diazepine in 42% yield. Interestingly a similar reaction of the monocyclic 3*H*-1,2-diazepine complex (**15a**) [containing no detectable amount of (**16a**)] gave both (**9a**) and (**10a**), further demonstrating the easy isomerisation in these systems.

(iii) *Structures and Spectra of the Dinuclear Iron Hexacarbonyl Complexes.*—The $^1H$ and $^{13}C$ n.m.r. spectra provided strong evidence that the diazepine ring had remained intact and that complexation was centred on the azo group. The spectra were similar to those of the parent diazepines but with changes in chemical shift values as illustrated in structures (**17**) and (**18**). It is notable that the absorptions due to the carbon atoms attached to the N–N linkage and those due to substituents at these positions are all shifted to lower frequency by complexation.

Complexation had a marked effect on the ease of ring inversion in both the 1*H*-2,3-benzodiazepine (**11a**)/(**12a**) and




(17) (18)

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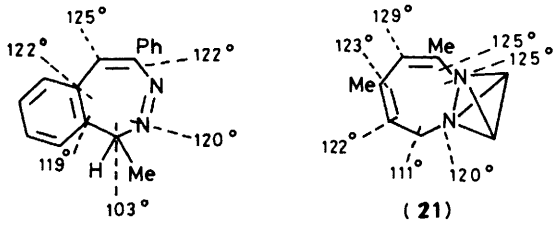



(20) (21)

the monocyclic systems (**9a**)/(**15a**) and (**9e**)/(**15e**). The benzodiazepine (**11a**) had a coalescence temperature for the 1-$H_2$ group of 102 °C ($\Delta G^{\ddagger}$ 72 kJ mol$^{-1}$); its complex (**12a**) had a value of −54 °C ($\Delta G^{\ddagger}$ 44.6 kJ mol$^{-1}$). This effect was more pronounced in the monocyclic systems: in these the diazepines are more resistant to ring inversion than their benzo analogues and the coalescence temperature cannot be reached because of thermal instability; thus for example in (**17**) [≡ (**9a**)] the methylene protons absorb at δ 2.0 and 5.8 and show some line broadening, indicating an approach to coalescence, at +130 °C. The activation energy for ring inversion must therefore be at least 77 kJ mol$^{-1}$. However the complex (**18**) [≡ (**15a**)] exhibited very easy ring inversion with chemical shift equivalence of the methylene protons at room temperature, separation into a pair of broad multiplets at δ 3.39 and 4.20 at −123 °C, and coalescence at −109 °C ($\Delta G^{\ddagger}$ 30.5 kJ mol$^{-1}$). The complex (**15e**) similarly had $T_c$ −105 °C ($\Delta G^{\ddagger}$ 31.4 kJ mol$^{-1}$). Thus in the monocyclic series complexation has reduced the activation energy for ring inversion by at least 45 kJ mol$^{-1}$. This must be related to the difference in the N–N bond length and the different angular requirements at the azo group in the diazepine and at the distorted $N_2Fe_2$ tetrahedron in the complex. Whereas the preferred angle at the azo group must be 120° the Me–N–N angles in (**6**) were found to be 123° by *X*-ray crystallography.[6] The structure of the complex (**15a**) has been determined by *X*-ray crystallography[7] and is shown in Figure 1. Unfortunately we do not have an *X*-ray structure for the uncomplexed monocyclic diazepine for direct comparison but the structure of the closely related benzodiazepine (**11b**) has been determined.[8] In both (**15a**) and (**11b**) the seven-membered ring adopts a boat conformation, but that of the complex (**19b**) is considerably flattened (as indicated by the angles shown) in comparison with the uncomplexed ring (**19a**). This flattening is also manifested in the larger internal ring angles in the complex: (**21**) *cf.* (**20**). Less angular distortion will therefore be required for it to attain the planar transition state for ring inversion which correlates with the lower activation energy observed.

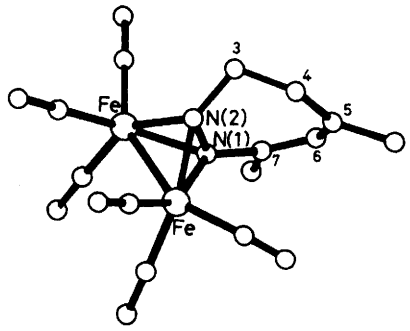
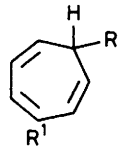



Figure 1.

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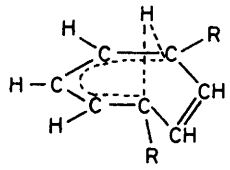


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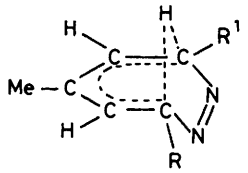



(24)

In the i.r. spectra of the complexes a multiplet pattern in the 1 950—2 050 cm$^{-1}$ region was observed for the carbonyl stretching vibrations, similar to those reported for other azo complexes of this type.[9] The characteristic three-band spectra of diene iron tricarbonyl complexes was not present and no absorptions were present in the double (1 750—1 850 cm$^{-1}$) or triple (1 620—1 730 cm$^{-1}$) bridging carbonyl regions.

(iv) *Effect of Complexation on* [1,5] *Sigmatropic Hydrogen Migration.*—As reported in section (ii), complexation of the azo group effectively stopped the easy [1,5] sigmatropic hydrogen shifts observed in the diazepine system (**9**) ⇌ (**10**). To rationalise this result it is necessary to look first at the uncomplexed diazepine and attempt to identify the factors which made the hydrogen migrations in that system so much faster (*ca.* $10^{10}$ times) than in the analogous hydrocarbon cycloheptatriene (**22**).

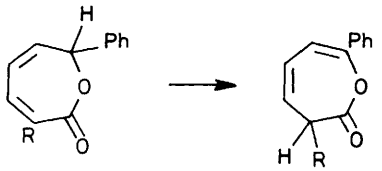
In the earlier report on the synthesis of these diazepines it was suggested that these hydrogen shifts were sigmatropic in character rather than intermolecular proton shifts because they took place readily in aprotic solvents in the absence of acids or bases. Further experimental work supports this contention. Thus a sample of the diazepine mixture (**9a**)/(**10a**), known to be in rapid dynamic equilibrium at room temperature,[1] was dissolved in deuteriochloroform containing a five-fold excess of perdeuteriomethanol and then monitored by $^1$H n.m.r. spectroscopy over a period of 24 h. No incorporation of deuterium into the diazepines was detected, thus ruling out any possibility of proton shifts either autocatalysed by the weakly basic azo group or mediated by adventitious traces of water.

The great enhancement of the rate of hydrogen migration by the formal replacement of a HC=CH group in (**22**) by an N=N group could be due to two effects: (*a*) changes in orbital energies and coefficients, and/or (*b*) a change in the structural geometry

**Table 3.** Distance of approach between migrating centres for [1,5] hydrogen shifts in cyclic conjugated diene systems

| Compound | Distance (Å)[a] C–C | C–H | Rate of migration |
|---|---|---|---|
| Cyclohexa-1,3-diene | 2.5 | 2.9 | Slow |
| Cyclohepta-1,3-diene | 2.8 | 2.6 | Medium |
| Cyclo-octa-1,3-diene | 3.0 | 2.5 | Medium |
| Cycloheptatriene | 2.8 | 2.7 | Medium |
| Cyclopentadiene | 1.5 | 2.2 | Very fast |
| 3*H*-1,2-Diazepine | 2.78 | 2.75 | Very fast |
| Iron carbonyl complex (**15a**) | 2.95 | 2.86 | |

[a] Measured on Dreiding models for the hydrocarbons and from *X*-ray structures of (**11b**) and (**15a**) for the diazepines.




(**25**) (**26**)

R = H or Me

of the ring. In considering (*b*) it should be noted that this type of explanation has been used before in rationalising differences in the rates of hydrogen shifts in cyclic conjugated dienes.[9] It can be seen from Table 3 that there is a good correlation between the C–H distance (migrating H to receiving C measured on Dreiding models at most favourable conformation) and rate for the hydrocarbons. However the differences between the diazepine and cycloheptatriene are marginal and it seems unlikely that steric factors make a major contribution to the greater rate in the diazepine.

The transition state for hydrogen migration in cycloheptatriene has been calculated[10] and is shown in (**23**); it has a planar pentadienyl unit with the other ethene bond out of plane and virtually out of conjugation. If the transition state for migration in the diazepine has a similar geometry (**24**) then the effects of conjugation to the out-of-plane azo group will be minimal, but it will still exert a strong electron-withdrawing effect at both ends of the pentadienyl system. The magnitude of this electron-withdrawing effect can be correlated with strong deshielding of C-3 (66 p.p.m.) and C-7 (154 p.p.m.) in the $^{13}C$ n.m.r. spectrum [structure (**17**)]. In the transition state (**23**) for the hydrogen shift in cycloheptatriene the dominant orbital interaction is that between $\psi_3$, the HOMO of the pentadienyl radical, and the 1s orbital of the hydrogen atom [Figure (2a)] which lies about 1β (−2.4 eV) below the zero level [Figure (2b)]. The stabilising effect of such a frontier orbital interaction is inversely proportional to the energy separation $\Delta E$. In the diazepine hydrogen shift (**24**) the effect of the electron-withdrawing azo group will be to lower the energy of $\psi_3$ [Figure (2c)] thus reducing the frontier orbital energy separation to $\Delta E'$ and stabilising the transition state.[11] The more rapid hydrogen migration in the diazepine thus accords with simple qualitative frontier orbital considerations. It is of interest to note a similar effect when the HC=CH in cycloheptatriene is replaced by –O–C(=O)–; thus the lactone (**25**) rapidly isomerises to give (**26**) above 4 °C.[12,13]

The observation that complexation of the azo group stops the hydrogen migration can be explained on the basis of either or both of the effects discussed above. It can be inferred from the $^{13}C$ n.m.r. chemical shifts of C-3 (55 p.p.m.) and C-7 (148 p.p.m.), as shown in structure (**18**), that complexation reduces the electron-withdrawing effect of the N–N unit (due presumably to considerable back donation from the metal to nitrogen). Thus the electronic rate-enhancing effect of the azo group will be diminished. Additionally, complex formation flattens the diazepine ring as discussed in section (ii) so that the approach distance between the 'migrating' hydrogen and C-7 is considerably increased (Table 3). These effects in combination suffice to make the hydrogen migration immeasurably slow even at 100 °C.

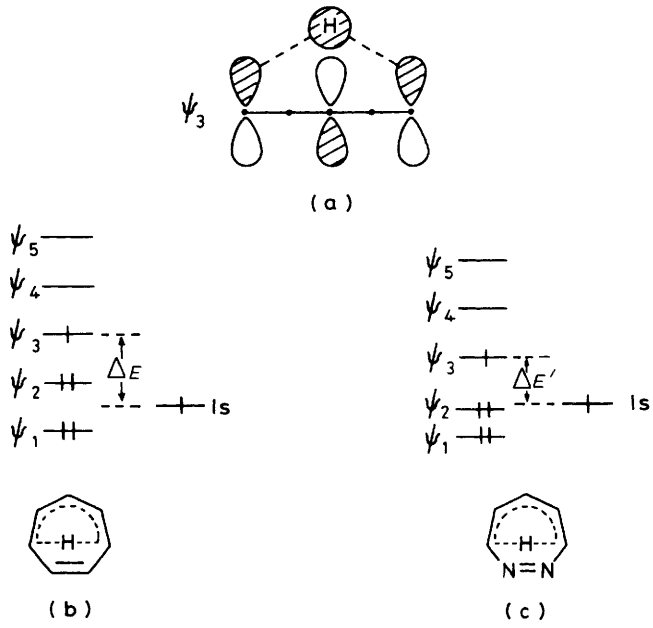



**Figure 2.**

## Experimental

$^1H$ N.m.r. spectra were obtained with a Varian EM360 (60 MHz) or HA100 (100 MHz) or a Bruker WH360 (360 MHz) spectrometer, and $^{13}C$ spectra with a Varian CFT20 (20 MHz) or Bruker WH360 (90.5 MHz) instrument. All samples were run as solutions in deuteriochloroform unless otherwise stated. Chemical shifts are recorded as δ values. Mass spectra were obtained with an A.E.I. MS902 spectrometer with electron ionisation at 70 eV unless otherwise stated. Preparative column chromatography on silica was carried out by the medium pressure technique (< 100 lb in$^{-2}$) 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), referred to here as 'petroleum', with varying proportions of ether. For chromatography on alumina material from Laporte Industries (Grade H, 100/200 mesh) deactivated to Grade III was used, with gravity elution. High performance liquid chromatography (h.p.l.c.) was carried out on a 25 × 0.5 cm column packed with Spherisorb S5Y; an ultra-violet detector (254 nm) was employed. 'Evaporation' of solvents indicates evaporation under reduced pressure by rotary evaporator.

The following compounds were prepared by literature routes: di-iron nonacarbonyl,[14] benzylideneacetone iron tricarbonyl complex,[15] 5,7-dimethyl- and 3,5-dimethyl-3*H*-1,2-diazepine,[1] 7-ethyl-3,5-dimethyl- and 3-ethyl-5,7-dimethyl-3*H*-1,2-diazepine,[1] 5-methyl-7-phenyl-3*H*-1,2-diazepine,[1] 4-phenyl-1*H*-2,3-benzodiazepine,[16] 1-methyl-4-phenyl-1*H*-2,3-benzodiazepine,[16] 1,2,3,3a-tetrahydro-10-phenylbenzo[*c*]cyclopenta-[*f*][1,2]diazepine.[17]

*Preparation of* 2,4-*Dienones*.—2,5-*Dimethylocta*-4,6-*dien*-3-*one*. A Grignard reagent prepared from isopropyl bromide (17.1 g, 0.139 mol) and magnesium (3.38 g, 0.139 mol) in ether (80 ml) was cooled to 0 °C and anhydrous cadmium chloride (12.7 g, 0.070 mol) was added in one batch. After rapid mechanical stirring for 30 min, 3-methylhexa-2,4-dienoic acid chloride[18] (8.0 g, 0.056 mol) in ether (30 ml) was added slowly. The mixture was boiled under reflux for 2 h, cooled to 0 °C, and hydrolysed with aqueous ammonium chloride (10% w/v; 120 ml). Extraction with ether, drying, and evaporation gave a yellow oil which was distilled to give 2,5-*dimethylocta*-4,6-*dien*-3-*one* as a yellow oil (2.88 g, 33%), b.p. 95—100 °C at 10 mmHg (Found: $M^+$, 152.119 333. $C_{10}H_{16}O$ requires *m/z*, 152.120 109); $\nu_{max.}$(film) 1 680 $cm^{-1}$ (C=O); $\delta_H$ (100 MHz) 1.08 (6 H, d, *J* 7 Hz, $Me_2CH$), 1.84 (3 H, d, *J* 5 Hz, 8-$H_3$), 1.98 and 2.22 (3 H, d, *J* 1.5 Hz, 5-Me), 2.62 (1 H, sept, *J* 7 Hz, 2-H), and 7.57 (d, *J* 16 Hz) and 5.9—6.4 (m) (3 H, olefinic); *E,E* to *Z,E* ratio *ca.* 2:1. The 2,4-*dinitrophenylhydrazone* had m.p. 137—138 °C (from ethanol) (Found: C, 57.6; H, 6.0; N, 16.8. $C_{16}H_{20}N_4O_4$ requires C, 57.8; H, 6.1; N, 16.9%).

1-*Phenyl*-5-*methylocta*-4,6-*dien*-3-*one*. A similar reaction using the Grignard reagent from phenethyl bromide (25.7 g, 0.139 mol) gave 1-*phenyl*-5-*methylocta*-4,6-*dien*-3-*one* (7.1 g, 60%), as a yellow oil, b.p. 140—145 °C at 0.05 mmHg (Found: $M^+$, 214.133 658. $C_{15}H_{18}O$ requires *m/z*, 214.135 758); $\nu_{max.}$(film) 1 685 $cm^{-1}$ (C=O); $\delta_H$ (100 MHz) 1.85 (3 H, d, *J* 4 Hz, 8-$H_3$), 1.95 and 2.23 (3 H, d, *J* 1.5 Hz, 5-Me), 2.85 (4 H, m, $CH_2CH_2$), 7.58 (d, *J* 16 Hz), and 5.8—6.3 (3 H, m, olefinic), and 7.05—7.30 (5 H, m, $C_6H_5$); *E,E* to *Z,E* ratio *ca.* 4:1. The 2,4-*dinitrophenylhydrazone* had m.p. 163—164 °C (from ethanol) (Found: C, 63.7; H, 5.6; N, 14.1. $C_{21}H_{22}N_4O_4$ requires C, 64.0; H, 5.6; N, 14.2%).

1-*Phenyl*-3-*methylhexa*-2,4-*dien*-1-*one*. A similar reaction using the Grignard reagent from bromobenzene (21.8 g, 0.139 mol) gave 1-*phenyl*-3-*methylhexa*-2,4-*dien*-1-*one* (6.4 g, 62%), as a yellow oil, b.p. 110 °C at 0.1 mmHg (Found: C, 83.9; H, 7.4. $C_{13}H_{14}O$ requires C, 83.8; H, 7.6%); $\nu_{max.}$(film) 1 680 $cm^{-1}$ (C=O); $\delta_H$ (100 MHz) 1.45 and 1.90 (3 H, d, *J* 4 Hz, 6-$H_3$), 2.13 and 2.30 (3 H, d, *J* 1.5 Hz, 3-Me), 6.10—6.30 (2 H, m, olefinic), 6.62 and 6.73 (2 H, br s), and 7.20—7.95 (5 H, m, $C_6H_5$); *E,E* to *Z,E* ratio *ca.* 3:1.

*Preparation of* 6,7-*Dihydro*-1-*tosyl*-1,2-*diazepines*.—6,7-*Dihydro*-5,7-*dimethyl*-3-*isopropyl*-1-*tosyl*-1,2-*diazepine* (**8d**). A mixture of 2,5-dimethylocta-4,6-dien-3-one (2.50 g, 16.4 mmol), tosylhydrazine (3.05 g, 16.4 mmol), and concentrated hydrochloric acid (1 ml) in ethanol (50 ml) was stirred at room temperature for 12 h. Sodium hydrogencarbonate was added to neutralise the acid and the solvent was evaporated off to leave a brown oil. Chromatography (silica; 25 vol % ether in petroleum) gave (i) 6,7-*dihydro*-5,7-*dimethyl*-3-*isopropyl*-1-*tosyl*-1,2-*diazepine* (1.42 g, 27%), m.p. 86—87 °C (from ethanol) (Found: C, 63.8; H, 7.6; N, 9.0. $C_{17}H_{24}N_2O_2S$ requires C, 63.7; H, 7.55; N, 8.7%); $\delta_H$ (100 MHz) 0.48 (3 H, d, *J* 7 Hz, 7-Me), 1.04 (3 H, d, *J* 7 Hz, isopropyl Me), 1.11 (3 H, d, *J* 7 Hz, isopropyl Me), 1.88 (3 H, br s, 5-Me), 2.18 (1 H, dd, *J* 18 and 2 Hz, 6-H), 2.98 (1 H, br dd, *J* 18 and 7 Hz, 6-H), 2.4 (3 H, s, tosyl Me), 2.53 (1 H, sept, *J* 7 Hz, $Me_2CH$), 4.7 (1 H, quint of d, *J* 7 and 2 Hz, 7-H), 5.7 (1 H, br s, 4-H), 7.24 (2 H, d, *J* 8 Hz, aromatic), and 7.86 (2 H, d, *J* 8 Hz, aromatic); $\delta_C$ (20 MHz) 12.6, 20.2, 26.8 (5-Me, 7-Me, tosyl Me); 21.4 ($CHMe_2$), 37.2 ($CHMe_2$), 44.6 (C-6), 51.3 (C-7), 120.0 (C-4), 134.7 (C-5), 160.6 (C-3), 128.6, 128.8, 143.4 (tert.), and 149.7 (tert.) (aromatic); and (ii) 2,5-*dimethylocta*-4,6-*dien*-3-*one tosylhydrazone* (0.57 g, 11%), m.p. 130—131 °C (from ethanol) (Found: C, 63.4; H, 7.4; N, 8.7. $C_{17}H_{24}N_2O_2S$ requires C, 63.7; H, 7.55; N, 8.7%); $\delta_H$ (100 MHz) 0.97 (6 H, d, *J* 6 Hz, $Me_2CH$), 1.53 (3 H, t, *J* 0.5 Hz, 5-Me), 1.8 (3 H, d, *J* 5 Hz, 7-Me), 2.38 (3 H, s, tosyl Me), 2.41 (1 H, sept, *J* 6 Hz, $Me_2CH$), 5.36 (1 H, br, s, 4-H), 5.83 (1 H, dq, *J* 15 and 5 Hz, 7-H), 6.1 (1 H, d, *J* 15 Hz, 6-H), 7.25 (2 H, d, *J* 8 Hz, aromatic), 7.77 (2 H, d, *J* 8 Hz, aromatic), and 7.41 (1 H, br s, NH).

6,7-*Dihydro*-5,7-*dimethyl*-3-*phenethyl*-1-*tosyl*-1,2-*diazepine* (**8c**). A mixture of 1-phenyl-5-methylocta-4,6-dien-3-one (4.6 g, 21.5 mmol), tosylhydrazine (4.0 g, 21.5 mmol) and concentrated hydrochloric acid (3 ml) in ethanol (50 ml) was stirred at room temperature for 12 h. Neutralisation with sodium hydrogencarbonate, drying ($MgSO_4$), and evaporation left a brown oil. Chromatography (alumina; 25 vol % ether in petroleum) gave 6,7-*dihydro*-5,7-dimethyl-3-*phenethyl*-1-*tosyl*-1,2-*diazepine* (5.20 g, 63%), m.p. 131—132 °C (from ethanol) (Found: C, 68.8; H, 6.8; N, 7.2. $C_{22}H_{26}N_2O_2S$ requires C, 69.1; H, 6.85; N, 7.3%); $\delta_H$ (100 MHz) 0.46 (3 H, d, *J* 7 Hz, 7-Me), 1.86 (3 H, br s, 5-Me), 2.18 (1 H, dd, *J* 18 and 2 Hz, 6-H), 2.96 (1 H, br dd, *J* 18 and 7 Hz, 6-H) (partly obscured by multiplet centred on 2.78), 2.40 (3 H, s, tosyl Me), 2.78 (4 H, m, $CH_2CH_2$), 4.74 (1 H, quint of d, *J* 7 and 2 Hz, 7-H), 5.71 (1 H, br s, 4-H), 7.15 (5 H, br s, $C_6H_5$), 7.25 (2 H, d, *J* 8 Hz, aromatic), and 8.85 (2 H, d, *J* 8 Hz, aromatic); $\delta_C$ (20 MHz) 12.5, 21.1, 26.5 (5-Me, 7-Me, tosyl Me); 33.0, 40.0, 44.4 (C-6 and $CH_2CH_2$); 51.5 (C-7), 120.6 (C-4), 134.5 (C-5), 154.9 (C-3); 149.8 (tert.), 143.2 (tert.), 141.0 (tert.), and 128.8, 128.2, 128.0, 127.9, 125.4 (aromatic).

6,7-*Dihydro*-5,7-*dimethyl*-3-*phenyl*-1-*tosyl*-1,2-*diazepine* (**8f**). A mixture of 1-phenyl-3-methylhexa-2,4-dien-1-one (3.80 g, 20.4 mmol), tosylhydrazine (3.80 g, 20.4 mmol) and concentrated hydrochloric acid (3 ml) in ethanol (30 ml) was stirred at room temperature for 12 h. The white solid was filtered off and crystallised from ethanol giving 6,7-*dihydro*-5,7-*dimethyl*-3-*phenyl*-1-*tosyl*-1,2-*diazepine* (4.30 g, 59%), m.p. 168—169 °C (Found: C, 67.9; H, 6.2; N, 8.0. $C_{20}H_{22}N_2O_2S$ requires C, 67.8; H, 6.3; N, 7.9%); $\delta_H$ (100 MHz) 0.60 (3 H, d, *J* 7 Hz, 7-Me), 1.98 (3 H, br s, 5-Me), 2.40 (1 H, dd, *J* 18 and 2 Hz, 6-H), 2.40 (3 H, s, tosyl Me), 3.18 (1 H, br d, *J* 18 and 7 Hz, 6-H), 4.84 (1 H, quint of d, *J* 7 and 2 Hz, 7-H), 6.23 (1 H, br s, 4-H), 7.15—7.70 (7 H, m, aromatic), and 7.88 (2 H, d, *J* 8 Hz, aromatic); $\delta_C$ (20 MHz) 13.4, 21.3, 27.1 (5-Me, 7-Me, and tosyl Me); 44.6 (C-6), 52.9 (C-7), 119.4 (C-4), 134.3 (C-5), 152.9 (C-3), 151.3 (tert.), 143.6 (tert.), 139.2 (tert.), and 129.1, 128.7, 128.6, 128.0, 127.1 (aromatic).

*Preparation of* 3H-1,2-*Diazepines*.—The general method was to heat the 6,7-dihydro-1-tosyl-1,2-diazepine with a two-fold molar excess of sodium ethoxide in dry toluene as described earlier.[1] After reaction the precipitate of sodium toluene-*p*-sulphinate was filtered off, the filtrate was washed with water and dried, and the toluene was evaporated off to leave a yellow oil. The last traces of toluene were removed by chromatography (alumina; 25 vol % ether in petroleum) and the resultant oil was distilled to give the diazepine or isomeric mixture of diazepines.

(i) 7-*Isopropyl*-3,5-*dimethyl*- *and* 3-*isopropyl*-5,7-*dimethyl*-3H-1,2-*diazepines* (**9d**)/(**10d**). 6,7-Dihydro-5,7-dimethyl-3-isopropyl-1-tosyl-1,2-diazepine (0.670 g, 2.1 mmol) (reaction time 5 min) gave after distillation a yellow oil (0.256 g, 74%), b.p. 90 °C at 0.2 mmHg, which consisted of a mixture of the two isomeric diazepines (Found: $M^+$, 164.130 303. Calc. for $C_{10}H_{16}N_2$: *m/z*, 164.131 342). The mixture could not be separated by h.p.l.c. using a 25 × 0.5 cm column packed with 5 μm Spherisorb (10 700 plates) and operated at 0 °C.[1] The n.m.r. absorptions were extracted from spectra of the mixture. 7-Isopropyl-3,5-dimethyl-3*H*-1,2-diazepine (**9d**); $\delta_H$ (360 MHz) 1.16 (3 H, d, *J* 7 Hz, isopropyl Me), 1.26 (3 H, d, *J* 7 Hz, isopropyl Me), 1.63 (1 H, br quint, *J* 6.5 Hz, 3-H), 1.96 (3 H, br s, 5-Me), 2.01 (3 H, d, *J* 6.5 Hz, 3-Me), 2.97 (1 H, sept, *J* 7 Hz, isopropyl CH), 4.90 (1 H, br d, *J* 5.5 Hz, 4-H), and 5.90 (1 H, br s, 6-H); $\delta_C$ (20 MHz) 18.4, 20.5, 21.5, 22.8 (3-Me, 5-Me, isopropyl $Me_2$); 33.6 ($Me_2CH$), 70.9 (C-3), 113.9 and 118.2 (C-4, C-6), 135.8 (C-5), and 164.9 (C-7). 3-Isopropyl-5,7-dimethyl-3*H*-1,2-diazepine (**10d**): $\delta_H$ (360 MHz)

1.19 (3 H, d, *J* 7 Hz, isopropyl Me), 1.23 (3 H, d, *J* 7 Hz, isopropyl Me), 1.96 (3 H, br s, 5-Me), 2.39 (3 H, s, 7-Me), 2.73 (1 H, d of sept, *J* 8.5 and 7 Hz, isopropyl CH), 5.01 (1 H, d, *J* 5.5 Hz, 4-H), and 5.90 (1 H, br s, 6-H) (H-3 not resolved); $\delta_C$ (20 MHz) 19.2, 19.7, 20.5, 20.9 (5-Me, 7-Me, isopropyl $Me_2$), 30.2 ($Me_2CH$), 82.0 (C-3), 115.6 and 117.1 (C-4, C-6), 136.3 (C-5), and 154.0 (C-7). The ratio of (**9d**) to (**10d**) was calculated as 34:66 from the integrals of the $^1$H n.m.r. spectrum.

(ii) 3,5-*Dimethyl*-7-*phenethyl*- *and* 5,7-*dimethyl*-3-*phenethyl*-3H-1,2-*diazepines* (**9c**)/(**10c**). A similar reaction (5 min) of 6,7-dihydro-5,7-dimethyl-3-phenethyl-1-tosyl-1,2-diazepine (3.15 g, 8.25 mmol) gave after distillation a yellow oil (1.73 g, 93%), b.p. 150 °C at 0.01 mmHg (Found: C, 79.7; H, 8.1; N, 12.3. $C_{15}H_{18}N_2$ requires C, 79.6; H, 8.0; N, 12.4%), which consisted of a mixture of the two diazepines. The mixture could not be separated by h.p.l.c. at 0 °C. N.m.r. spectra: $\delta_H$ (360 MHz) 1.53 [1 H, br quint, *J* 6 Hz, 3-H of (**9c**)], 1.64 [1 H, br q, *J* 6 Hz, 3-H of (**10c**)], 1.89 and 1.93 [3 H, t, *J* 1 Hz, 5-Me of (**10c**) and (**9c**)], 1.98 [3 H, d, *J* 6 Hz, 3-Me of (**9c**)], 2.37 [3 H, s, 7-Me of (**10c**)], 2.57, 2.81, 3.04, 3.24 [2 H, m, $PhCH_2CH_2$ in (**10c**) and (**9c**)], 2.91 [2 H, m, $PhCH_2CH_2$ in (**10c**) and (**9c**)], 4.88 and 4.95 [1 H, br d, *J ca.* 6 Hz, 4-H in (**10c**) and (**9c**)], 5.82 and 5.88 [1 H, br s, 6-H in (**10c**) and (**9c**)], and 7.12—8.31 (5 H, m, $C_6H_5$); $\delta_C$ (20 MHz) 18.1, 20.1, 20.2, 20.6 (4 × Me), 32.1, 34.1, 35.0, 36.8 (4 × $CH_2$), 70.8 and 74.8 (C-3), 116.2, 117.0, 117.1, 118.3 (C-4 and C-6); 125.5, 125.7, 127.9, 128.0, 128.1, 135.4 (tert.), 136.0 (tert.), 140.4 (tert.), 141.2 (tert.) (C-5 and aromatics), and 154.2 and 154.7 (C-7).

(iii) 3,5-*Dimethyl*-7-*phenyl*-3H-1,2-*diazepine* (**9f**). A similar reaction (5 min) of 6,7-dihydro-5,7-dimethyl-3-phenyl-1-tosyl-1,2-diazepine (2.27 g, 6.41 mmol) gave after distillation 3,5-*dimethyl*-7-*phenyl*-3H-1,2-*diazepine* as a yellow oil (1.07 g, 84%), b.p. 145 °C at 0.2 mmHg. Crystallisation from petroleum (b.p. 40—60 °C) at −30 °C gave yellow prisms, m.p. 45—46 °C (Found: C, 79.0; H, 7.2; N, 14.0. $C_{13}H_{14}N_2$ requires C, 78.75; H, 7.1; N, 14.1%); $\delta_H$ (360 MHz) 1.92 (1 H, br quint, *J* 6 Hz, 3-H), 2.05 (3 H, t, *J* 1 Hz, 5-Me), 2.05 (3 H, d, *J* 6 Hz, 3-Me), 5.08 (1 H, dq, *J* 6 and 1 Hz, 4-H), 6.35 (1 H, br s, 6-H), 7.25—7.50 (3 H, m, aromatic), and 7.78—7.82 (2 H, m, aromatic); $\delta_C$ (20 MHz) 18.2, 20.8 (2 × Me), 72.1 (C-3), 115.4 and 118.9 (C-4, C-6), 125.8, 128.4, 128.6, 136.7 (tert.), 136.8 (tert.) (C-5 and aromatic), and 156.3 (C-7).

*Conversion of* 1H-2,3-*Benzodiazepines*, 3H-1,2-*Benzodiazepines, and* 3H-1,2-*Diazepines into Di-iron Hexacarbonyl Complexes*.—The complexes were prepared by dissolving the diazepine and a two-fold molar excess of di-iron nonacarbonyl in dry degassed benzene and stirring the solution at room temperature for 24 h. The mixture was then filtered through Celite and the filtrate was evaporated under reduced pressure to leave a red oil. Chromatography on alumina (petroleum) gave the complex as a red crystalline solid.

(i) 4-*Phenyl*-1H-2,3-*benzodiazepine* (**11a**). The benzodiazepine (1.5 g, 6.8 mmol) gave the *complex* (**12a**) (1.18 g, 53%), m.p. 158—160 °C (decomp.) (Found: C, 50.5; H, 2.4; N, 5.7. $C_{21}H_{12}Fe_2N_2O_6$ requires C, 50.4; H, 2.4; N, 5.6%); $\delta_H$ (100 MHz; 23 °C) 4.48 (2 H, s, 1-$H_2$), 6.60 (1 H, s, 5-H), and 7.15—7.55 (9 H, m, aromatic); at −83 °C 1-$H_2$ gave a pair of doublets, 4.19 (1 H, d, *J* 14 Hz) and 4.77 (1 H, d, *J* 14 Hz), $T_c$ −54 °C; $\delta_C$ (20 MHz) 61.6 (C-3), 117.9 (C-5), 126.2, 128.3, 128.6, 129.0, 129.3, 129.7, 135.0 (tert.), 136.5 (tert.), 138.7 (tert.), (aromatic), 149.3 (C-4), and 209.6 (C=O); *m/z* 56 (32), 112 (24), 117 (22), 173 (31), 192 (24), 205 (22), 229 (75), 305 (37), 332 (18), 360 (100), 388 (59), 416 (20), 444 (8), 472 (34), and 500 (25%).

(ii) 1-*Methyl*-4-*phenyl*-1H-2,3-*benzodiazepine* (**11b**). The benzodiazepine (0.317 g, 1.35 mmol) gave after 12 h the *complex* (**12b**) (0.406 g, 58%), m.p. 165—168 °C (decomp.) (Found: C, 51.7; H, 2.7; N, 5.6. $C_{22}H_{14}Fe_2N_2O_6$ requires C, 51.4; H, 2.7; N, 5.45%); $\delta_H$ (100 MHz) 1.7 (3 H, d, *J* 7 Hz, 1-Me), 4.18 (1 H, q, *J* 7 Hz, 1-H), 6.61 (1 H, s, 5-H), and 7.1—7.55 (9 H, m, aromatic); $\delta_C$ (20 MHz) 15.8 (Me), 61.0 (C-3), 118.1 (C-5); 124.9, 126.0, 128.3, 128.5, 129.0, 129.7, 136.2 (tert.), 137.5 (tert.), 138.5 (tert.) (aromatic), 149.1 (C-4); and 182.2, 182.5 (C=O).

(iii) 1,2,3,3a-*Tetrahydro*-10-*phenylbenzo*[c]*cyclopenta*[f]-[1,2]*diazepine* (**13**). The benzodiazepine (0.192 g, 0.74 mmol) gave the *complex* (**14**) (0.229 g, 57%), m.p. 164—166 °C (from pentane) (Found: C, 53.2; H, 3.0; N, 5.0. $C_{24}H_{16}Fe_2N_2O_6$ requires C, 53.4; H, 3.0; N, 5.2%); $\delta_H$ (100 MHz) 1.77—2.26 and 2.5—2.78 (6 H, m, cyclopentyl $CH_2$), 3.72 (1 H, br d, *J* 7 Hz, 3a-H), 6.74 (1 H, d, *J* 8 Hz, aromatic), and 6.95—7.50 (8 H, m, aromatic); $\delta_C$ (20 MHz) 24.5, 31.3, 34.1 (C-1, C-2, C-3), 67.2 (C-3a); 126.0, 127.6, 128.0, 128.4, 128.8, 129.9, 130.9, 132.9 (tert.), 136.8 (tert.), 140.7 (tert.), 145.0 (tert.), 147.2 (tert.) (aromatic and olefinic), and 210.0 (C=O).

(iv) 5-*Methyl*-7-*phenyl*-3H-1,2-*diazepine* (**9e**). The diazepine (0.786 g, 2.16 mmol) gave the *complex* (**15e**) (0.141 g, 28%), m.p. 119—120 °C (from pentane) (Found: C, 46.7; H, 2.6; N, 6.1. $C_{18}H_{12}Fe_2N_2O_6$ requires C, 46.6; H, 2.6; N, 6.0%); $\delta_H$ (100 MHz) 1.93 (3 H, s, Me), 3.90 (2 H, d, *J* 6 Hz, 3-$H_2$), 5.86 (1 H, br t, *J* 6 Hz, 4-H), 5.90 (1 H, s, 6-H), and 7.15—7.40 (5 H, m, aromatic); at 360 MHz, −120 °C in arcton 3-$H_2$ gave two broad peaks at δ 3.64 and 4.38, $T_c$ −105 °C; $\delta_C$ (20 MHz) 22.8 (Me), 55.7 (C-3); 118.7, 126.1, 128.2, 129.1, 138.5 (tert.), 142.3 (tert.), 151.6 (tert.) (C-4 to C-7 and aromatics), and 210.0 (C=O).

(v) 3,5-*Dimethyl*- *and* 5,7-*dimethyl*-3H-1,2-*diazepine mixture* (**10a**)/(**9a**). (*a*) The diazepine mixture (15:85) (1.5 g, 12.3 mmol) gave only the 5,7-*dimethyl*-3H-1,2-*diazepine complex* (**15a**) (1.51 g, 31%), m.p. 122—123 °C (from hexane) (Found: C, 38.7; H, 2.4; N, 6.7. $C_{13}H_{10}Fe_2N_2O_6$ requires C, 38.8; H, 2.5; N, 7.0%); $\delta_H$ (100 MHz) 1.84 (3 H, s, 5-Me), 1.97 (3 H, s, 7-Me), 3.76 (2 H, d, *J* 6 Hz, 3-$H_2$), 5.48 (1 H, br s, 6-H), and 5.72 (1 H, br t, 4-H); at 360 MHz, −143 °C in arcton 3-$H_2$ gave two broad multiplets at δ 3.39 and 4.20, $T_c$ −109 °C; $\delta_C$ (20 MHz) 22.7, 23.0 (2 × Me), 55.2 (C-3); 117.0, 124.8 (C-4, C-6); 142.3, 148.2 (C-5, C-7), and 210.1 (C=O). The product was examined by $^1$H n.m.r. spectroscopy both before and after chromatography and by h.p.l.c. using silica and reverse-phase (ODS) columns but no complex of the other diazepine isomer was detected.

(*b*) The diazepine mixture (0.200 g, 1.6 mmol) and benzylideneacetone iron tricarbonyl complex (0.500 g, 1.7 mmol) in dry degassed benzene (20 ml) were heated at 55—60 °C for 48 h. Evaporation and chromatography gave (**15a**) (0.206 g, 64%) identical with that obtained in (*a*).

(vi) 7-*Ethyl*-3,5-*dimethyl*- *and* 3-*ethyl*-5,7-*dimethyl*-3H-1,2-*diazepine mixture* (**9b**)/(**10b**). The diazepine mixture (1.01 g, 6.73 mmol) (51:49) gave a mixture of the complexes (**15b**) and (**16b**) in the ratio 60:40 (1.34 g, 46%), m.p. 72—73 °C (Found: C, 42.0; H, 3.2; N, 6.5. Calc. for $C_{15}H_{14}Fe_2N_2O_6$: C, 41.9; H, 3.3; N, 6.5%); $\delta_H$ (360 MHz) 1.03 [t, *J* 7.5 Hz, $CH_3CH_2$ of (**16b**)], 1.12 [t, *J* 7.5 Hz, $CH_3CH_2$ of (**15b**)], 1.33 [d, *J* 6.5 Hz, 3-Me of (**15b**)], 1.55—1.80 [m, $CH_3CH_2$ of (**16b**)], 1.83 [m, 5-Me of (**15b**) and (**16b**)], 1.98 [s, 7-Me of [**16b**)], 2.10—2.35 [m, $CH_3CH_2$ of (**15b**)], 3.20 [m, 3-H of (**16b**)], 3.47 [br quint, *J ca.* 6 Hz, 3-H of (**15b**)], 5.44 [s, 6-H of (**15b**)], 5.49 [d, *J ca.* 6 Hz, 4-H of (**15b**)], 5.49 [s, 6-H of (**16b**)], and 5.52 [br d, *J ca.* 6 Hz, 4-H of (**16b**)]; $\delta_C$ (20 MHz) 9.8, 12.9, 17.5, 22.7, 22.9 (3-Me, 5-Me, 7-Me and $CH_3CH_2$); 25.1, 30.7 (2 × $CH_3CH_2$) 59.3 [C-3 of (**15b**)], 64.2 [C-3 of (**16b**)]; 115.2 and 129.7 [C-4 and C-6 of (**15b**)]; 116.9 and 128.5 [C-4 and C-6 of (**16b**)], 139.8 [C-5 of (**15b**)], 140.3 [C-5 of (**16b**)], 148.3 [C-7 of (**16b**)], 153.5 [C-7 of (**15b**)]; and 210.1 and 210.3 (C=O).

(vii) 7-*Isopropyl*-3,5-*dimethyl*- *and* 3-*isopropyl*-5,7-*dimethyl*-3H-1,2-*diazepine mixture* (**9d**)/(**10d**). The diazepine mixture (0.165 g, 1.0 mmol) gave a mixture of the two complexes (**15d**) and (**16d**) in the ratio 88:12 (0.253 g, 57%), m.p. 64—65 °C (from pentane) (Found: C, 43.2; H, 3.7; N, 6.3. Calc. for

$C_{16}H_{16}Fe_2N_2O_2$: C, 43.3; H, 3.6; N, 6.3%). The following n.m.r. absorptions were derived from spectra of the mixture. Complex (**15d**): $\delta_H$ (360 MHz) 1.13 (3 H, d, *J* 7 Hz, isopropyl Me), 1.15 (3 H, d, *J* 7 Hz, isopropyl Me), 1.34 (3 H, d, *J* 6.5 Hz, 3-Me), 1.83 (3 H, br s, 5-Me), 2.37 (1 H, sept, *J* 7 Hz, $Me_2CH$), 3.44 (1 H, br quint, *J ca.* 6 Hz, 3-H), 5.42 (1 H, s, 6-H), and 5.49 (1 H, br d, *J ca.* 6 Hz, 4-H); $\delta_C$ (20 MHz) 17.7, 21.1, 22.8, 23.3 (3-Me, 5-Me, $CHMe_2$), 36.4 ($CHMe_2$), 59.4 (C-3); 113.9, 129.6 (C-4, C-6); 139.8 (C-5), 157.5 (C-7), and 181.6 (C=O). Complex (**16d**): $\delta_H$ (360 MHz) 0.98 (3 H, d, *J* 7 Hz, isopropyl Me), 1.00 (3 H, d, *J* 7 Hz, isopropyl Me), 1.85 (3 H, s, 5-Me), 1.99 (3 H, s, 7-Me), 2.04 (1 H, m, $CHMe_2$), 3.06 (1 H, m, 3-H), 5.52 (1 H, s, 6-H), and 5.61 (1 H, br d, *J ca.* 5 Hz, 4-H); $\delta_C$ (20 MHz) 16.4, 20.1, 23.0, 30.3 (3-Me, 5-Me, $CHMe_2$), 36.0 ($CHMe_2$), 67.0 (C-3); 117.2 and 125.9 (C-4, C-6), and 181.9 (C=O) (C-5 and C-7 not observed because of low concentration of this isomer).

(viii) 3,5-*Dimethyl*-7-*phenethyl*- *and* 5,7-*dimethyl*-3-*phenethyl*-3H-1,2-*diazepine mixture* (**9c**)/(**10c**). The diazepine mixture (51:49) (0.600 g, 2.65 mmol) gave a mixture of the complexes (**15c**) and (**16c**) in the ratio 72:28 (0.514 g, 38%), m.p. 64—65 °C (from hexane) (Found: C, 49.6; H, 3.6; N, 5.5. Calc. for $C_{21}H_{18}Fe_2N_2O_6$: C, 49.8; H, 3.6; N, 5.5%). The isomers were separated by h.p.l.c. using a 25 × 0.7 cm column packed with 5 μm Spherisorb silica (*ca.* 9 000 plates) and hexane as eluant. Multiple injections (5 μl) of a *ca.* 0.2M-solution gave (i) (**15c**) (0.006 g), $\delta_H$ (360 MHz) 1.34 (3 H, d, *J* 7 Hz, 3-Me), 1.72 (3 H, s, 5-Me), 2.51 (2 H, m, $PhCH_2CH_2$), 2.71 (1 H, m, $PhCH_2CHH$), 2.83 (1 H, m, $PhCH_2CHH$), 3.49 (1 H, br m, 3-H), 5.33 (1 H, s, 6-H), 5.48 (1 H, br m, 4-H), and 7.15—7.35 (5 H, m, aromatic); and (ii) (**16c**) (0.002 g), $\delta_H$ (360 MHz) 1.85 (3 H, s, 5-Me), 1.96 (3 H, s, 7-Me), 1.9—2.0 (2 H, m, $PhCH_2CH_2$), 2.65—2.85 (2 H, m, $PhCH_2CH_2$), 3.28 (1 H, m, 3-H), 5.47 (1 H, s, 6-H), 5.57 (1 H, br d, *J* 4 Hz, 4-H), and 7.15—7.35 (5 H, m, aromatic); $\delta_C$ (mixture) (20 MHz) 17.6, 22.5, 22.8, 23.0 (4 × Me); 31.6, 33.7, 35.1, 40.4 ($CH_2CH_2$); 59.4, 62.4 (C-3); 116.9, 117.4, 126.2, 128.2, 128.4, 130.0, 139.8 (tert.), 140.1 (tert.), 140.5 (tert.) (C-4 to C-6 and aromatic); 148.4; 150.5 (C-7); and 210, 210.3 (C=O).

*Thermolysis Study.*—The complex of 3,5-dimethyl-7-phenethyl-3*H*-1,2-diazepine (**15c**) (1.0 mg) was dissolved in dry toluene and heated for successive periods of 15 min at each of the temperatures 50, 65, 80, and 85 °C and finally for 2 h at 110 °C. The reaction was monitored by h.p.l.c. which showed that no isomerisation to the complex (**16c**) occurred but the reactant did decompose at 110 °C. A similar experiment carried out on the complex of 5,7-dimethyl-3-phenethyl-3*H*-1,2-diazepine (**16c**) similarly showed no isomerisation to (**15c**).

*Disengagement of Diazepine Di-iron Hexacarbonyl Complexes.*—4-*Phenyl*-1H-2,3-*benzodiazepine complex* (**12a**). This was carried out by Shvo's method.[19] The complex (0.645 g, 1.29 mmol) and freshly sublimed trimethylamine *N*-oxide (1.78 g, 25.8 mmol) in dry benzene (20 ml) were stirred at room temperature for 12 h. Evaporation and chromatography (alumina; 10 vol % ether in petroleum) gave the benzodiazepine (0.120 g, 42%), m.p. 130—132 °C (from ethanol) (lit.,[16] 132—133 °C).

5,7-*Dimethyl*-3H-1,2-*diazepine complex* (**15a**). A reaction similar to that above gave 3,5-dimethyl-3*H*-1,2-diazepine (**10a**) and 5,7-dimethyl-3*H*-1,2-diazepine (**9a**) as an equilibrium mixture in 39% yield. H.p.l.c. monitoring during the reaction showed the presence of both isomers.

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