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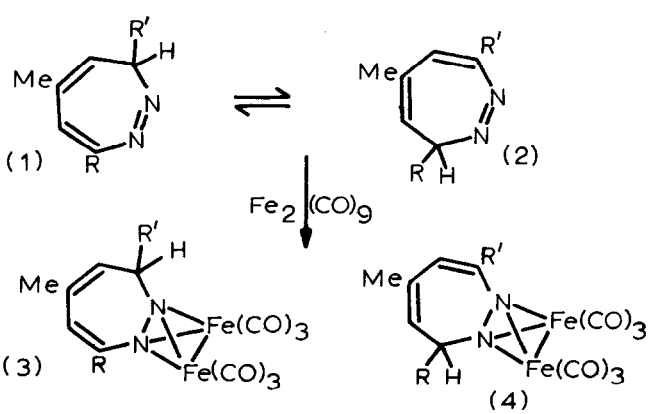
DINUCLEAR IRON CARBONYL COMPLEXES OF 3H-1,2-DIAZEPINES

Carl B. Argo and John T. Sharp*
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

Abstract. 3H-1,2-Diazepines (1/2) give dinuclear complexes (3/4) on reaction with diiron nonacarbonyl. Complexation much reduces the rate of the [1,5] sigmatropic hydrogen shift across the diazepine ring and also reduces the activation energy for ring inversion.

We have recently reported the first synthesis of 3H-1,2-diazepines[1] e.g. (1) and (2). This is an interesting ring system because of the fast [1,5] sigmatropic hydrogen migrations which interconvert (1) and (2). These hydrogen shifts are much faster than for analogous carbocyclic rings and prevent isolation of the isomers at room temperature, e.g. $t_{\frac{1}{2}}$ for (2c) is ca 30 minutes at 0°C.

We initiated this study of metal complex formation by the diazepines in the hope that complexes could be prepared in which the diazepine ring remained intact but with a much reduced rate for the hydrogen shifts so that complexes of the isomers (1) and (2) could be separated for characterisation, spectroscopic study, and possibly for low temperature regeneration of the diazepines. This preliminary report on the reaction of the diazepines with di-iron nonacarbonyl describes the nature of the products and the effect of complexation on both the rate of the hydrogen shift and the ease of inversion of the diazepine ring. Previous work with 1H-1,2-diazepines has shown that they form π-complexes via attachment of the $Fe(CO)_3$ moiety to the butadiene unit of the diazepine ring.[2] This work shows that the reactivity of the 3H-1,2-diazepines is quite different and involves an organo-metallic interaction by the azo-group only to give complexes (3/4) containing the tetrahedral Fe_2N_2 system, similar to those previously reported for some other azo-compounds.[3] The structure of (3c) has been confirmed by X-ray diffraction.[4]



a; R=R'=Me
b; R=Ph, R'=H
c; R=Me, R'=H
d; R=Me, R'=Et
e; R=Me, R'=Pr^i
f; R=Me, R'=CH_2CH_2Ph

The diazepines reacted readily with di-iron nonacarbonyl at room temperature to give the complexes in moderate yield (28-57%) but conversions were improved by the use of benzylideneacetone iron tricarbonyl as the reagent, for example the yield of (3c) increased from 31 to 64%. The diazepines (1/2 a,b, and c) gave single products (3 a,b,c); this is perhaps not surprising for (1/2b) which contains no detectable (2b) at equilibrium but more so for (1/2c) which contains ca 15% of (2c). Examination of the reaction mixture by h.p.l.c. and of the crude chromatographed product by n.m.r. failed to reveal any complex of (2c) so it appears that this diazepine is at least ca 3x less reactive than its isomer. The other diazepines (d-f) gave both (3) and (4). It has not yet proved possible to separate the isomers (3/4d) and (3/4e) but (3f) and (4f) have been separated on a small scale by column chromatography (25 x 0.5 cm, 5 μm Hypersil, 11,000 plates, elution with 50% water-saturated hexane).

Unlike the diazepines (1)/(2) which interconvert rapidly at room temperature the complexes (3f) and (4f) were stable to isomerisation at 110°C but did decompose slowly at this temperature. Thus it is clear that the complexation of the azo-group has much reduced its rate-enhancing effect on the [1,5] sigmatropic hydrogen shift across the diazepine ring. This effect is probably largely related to the change in the electronic effect of the diaza unit brought about by complexation but may also be partly steric in origin since the X-ray derived structure of the complex shows that the ring is slightly flattened leading to a greater C-7 to H-3 distance (2.86Å) than that measured on a Dreiding model (2.60Å) of the diazepine itself.

A variable temperature ^{1}H n.m.r. study on the complexes (3b) and (3c) has shown that complexation also much reduces the activation energy for ring inversion. The thermal instability of the diazepines themselves prevents measurement of the coalescence temperature for the methylene absorptions, but for (1c) the rate of ring inversion is still slow at 120°C. At this temperature there is some broadening of the methylene peaks but it is well below the coalescence temperature, thus $\Delta G^{\ddagger}$ must be > 75kJ mol^{-1}. For the complexes (3c) and (3b) the coalescence temperatures for the methylene group (at 360 MHz) are -108° and -105°C respectively giving $\Delta G^{\ddagger}$ values of 30.7 and 31.4 kJ mol^{-1}.

The diazepines can be regenerated in moderate yield from their complexes by mild oxidation with Shvo's reagent[5] at room temperature but we have not yet been able to do this at temperatures low enough to usefully inhibit the (1)$\rightleftarrows$(2) interconversion reaction.

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References

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