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REACTION OF TRANSITION METAL CARBONYLS WITH HETEROCYCLIC SYSTEMS

V *. THE REACTION OF $Fe_2(CO)_9$ WITH BICYCLIC 1,2-OXAZINE COMPOUNDS

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Summary

A study of the reactions of $Fe_2(CO)_9$ towards the $\geq$N—O bond has extended 9-phenyl-9-aza-8-oxabicyclo[3.2.2]nona-6-ene (I) and 8-phenyl-9-aza-7-oxabicyclo[4.2.1]nona-2,4-diene (II). The reactions are complete after 1 h at 40—50°C. Apart from the corresponding anilino alcohols, the products lack the oxygen atom of the $\geq$N—O bond. The stereochemistry of the products is indicative of an intramolecular process. Mechanistic proposals are based on an initial oxidative insertion of iron into the $\geq$N—O bond, followed by several competing reactions.

Introduction

Reactions of the $\geq$N—O bond with iron carbonyls have been described in several publications [1—4]. Although a definite reaction pattern emerged, the distribution of the various products depends to a large extent on the structure of the organic substrate. The study described below was concerned with examining the structure-reactivity relationships and the mechanism of the reactions.

The reagents used for the studies were 9-phenyl-9-aza-8-oxabicyclo[3.2.2]-nona-6-ene (I) and 8-phenyl-9-aza-7-oxabicyclo[4.2.1]nona-2,4-diene (II). Both possess $\geq$N—O functionality, and underwent complete reaction when treated with $Fe_2(CO)_9$ in benzene at 40—50°C for 1 h.

Results

The products obtained by reactions 1—4 are new. Considerable effort was expended on their structural and stereochemical elucidation.

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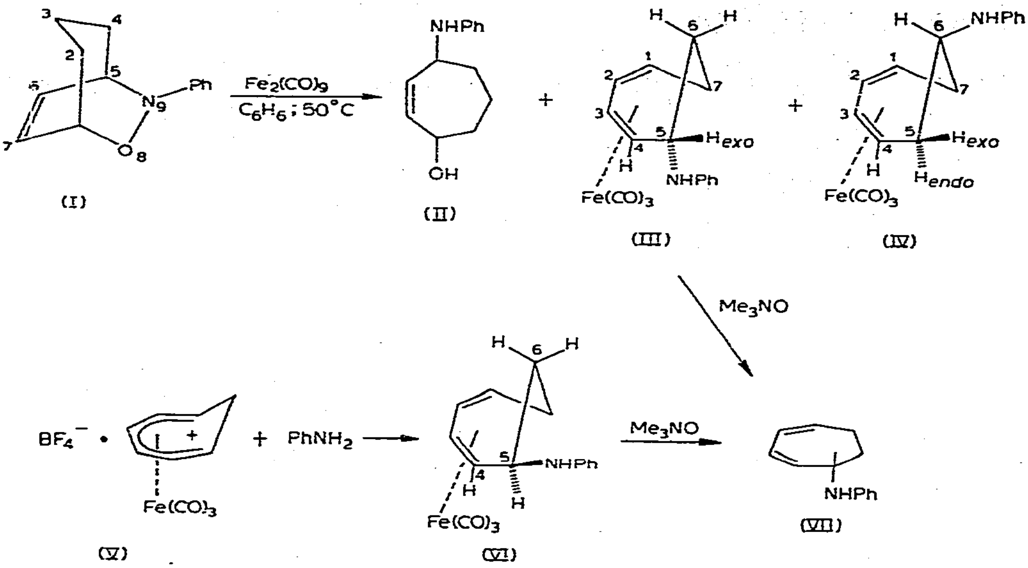
* For parts I—IV see refs. 1—4.

Reaction of I with $Fe_2(CO)_9$ (eq. 1)

The heterobicyclic I was obtained by a 1,4-cycloaddition reaction of PhNO to 1,3-cycloheptadiene. Three products (eq. 1) were isolated from the reaction of I and $Fe_2(CO)_9$.

The iron-free *cis*-4-anilinocyclohept-2-ene-1-ol (II) was isolated (30%) and found to be identical with the product from the chemical reduction of I (Zn/HAc). The *cis* configuration follows from the latter reaction.



(I) (II) (III) (IV) (1)

(V) (VI) (VII) (2)

$$\text{VII} + Fe_2(CO)_9 \longrightarrow \text{III} + \text{IV} + \text{VI} \qquad (3)$$

Two iron complexes, which were assigned structures III and IV (vide infra), were separated chromatographically. Elemental analysis and mass spectral data indicated that these are isomeric anilino cycloheptadieneiron tricarbonyl complexes. Provided that the anilino group is attached to an sp^3 carbon atom (NMR spectra exhibited signals from 4 vinylic protons) four isomers must be considered. These are the *endo*- and *exo*-isomers of 5- and 6-anilinocyclohepta-1,4-dieneiron tricarbonyl. The structural assignments of III and IV are described below.

exo-5-Anilinocyclohepta-1,4-dieneiron tricarbonyl (VI) was prepared by treating the cycloheptadienylium cation V with aniline (eq. 2). It is known [5] that nucleophiles attack such cations from the opposite side of the metal, thus leading to *exo* stereochemistry in the product VI. Complex VI is not identical with either III or IV. Treatment of VI or III with Me_3NO/acetone [6] at room temperature produced the same product 5-anilinocyclohepta-1,4-diene (VIII). Similar treatment of compound IV, produced a different substance (TLC). It follows that III and VI are diastereomers of 5-anilinocyclohepta-1,3-dieneiron tricarbonyl. Since VI was shown to possess the *exo* configuration, it follows that III is the *endo* isomer as depicted in eq. 1.

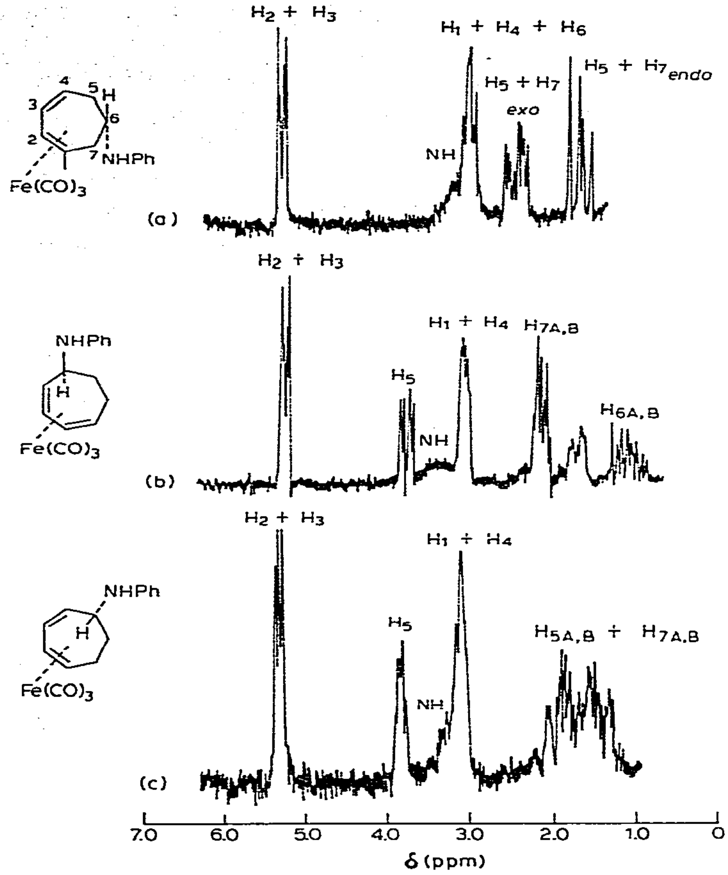


Fig. 1. NMR spectra at 100 MHz in $CDCl_3$ (TMS internal reference) of (a) IV, (b) VI and (c) III. Aromatic signals are omitted.

The above assignment was supported by NMR data which was subsequently used for the structural assignment of IV and other compounds. The NMR spectra of III, IV and VI are presented in Fig. 1 with the appropriate assignments of the signals made by extensive spin-decoupling experiments. Such decoupling experiments indicate that H(4) and H(5) of III (Fig. 1c) are spin coupled (J 5 Hz), while the coupling of the same protons in VI is absent (Fig. 1b). This behaviour is in complete agreement with the structural assignments and accounted for by the dihedral angles (H(4)—H(5)) of 0 and 90° in III and VI respectively. The clear quartet of H(5) which appears in the spectrum of VI (Fig. 1b) is the X part of an ABX system, in which AB represents H(6)-*endo* and H(6)-*exo* protons. Consequently $J_{5,6\,endo}$ 4 Hz and $J_{5,6\,exo}$ 11 Hz, in agreement with the corresponding dihedral angles of H(5) and the two H(6) protons of VI. The above two coupling constants were generated by the separate irradiations of the high and low field branches of H(6) (Fig. 1b) and observing the collapsing of the H(5) signals into two different doublets. The fact that the H(5) signal of III (Fig. 1c) is substantially narrower than that of H(5) in VI (Fig. 1b) is due to the absence of the large *anti*-parallel H(5)—H(6) spin interaction present in the former and absent in the latter compound.

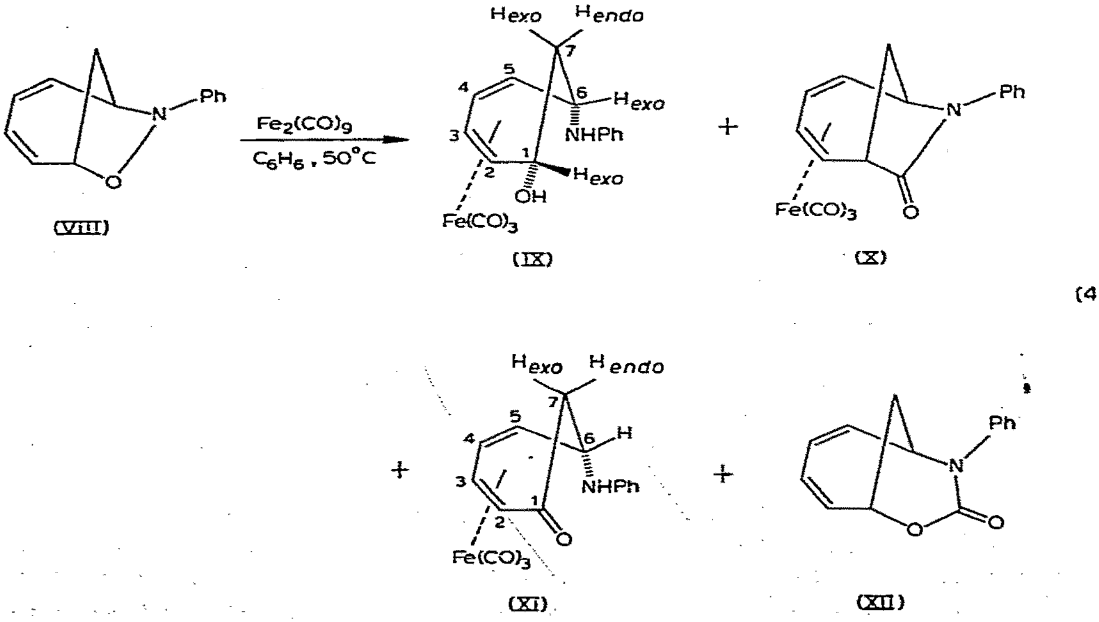
From the above argument it follows that the second complex isolated from the reaction (eq. 1) is a 6-anilino isomer, and its *endo* configuration (IV) was assigned on the basis of the following NMR observations (Fig. 1a):

(a) The high field 4-signal pattern, which integrates for 2 protons, was identified as an A_2 branch of an A_2B_2X system (H(5); H(6), H(7)). This A_2 branch was assigned to H(5)-*endo* and H(7)-*endo* of IV (structure IV possesses a plane of symmetry). The observed two large coupling constants, J 17 and 12 Hz, are assigned to the geminal and H(6) spin interactions, respectively. It is on the basis of the magnitude of the latter J value (12 Hz) that the *exo* configuration was assigned to H(6) in IV. A similar value (11 Hz) was recorded for the same spin interaction in VI. Consequently, the anilino group at C(6) in IV must possess the *endo* configuration, as depicted in the structural formula IV.

(b) As noted (Fig. 1a) H(1), H(4) and H(6) resonate at the same field value. Irradiation at the center of the complex signal transformed the multiple high field AB pattern to a sharp 4-line A_2B_2 spectrum (J 17 Hz). This behaviour, inter alia, corroborates the above assignments of the signals.

Reaction of VIII with $Fe_2(CO)_9$ (eq. 4)

The (2 + 6) cyclo-addition product of nitrosobenzene and cycloheptatriene (VIII) was treated with $Fe_2(CO)_9$ in the usual way. The complicated mixture of products was resolved only with difficulty into pure products, and the rather low yields of pure products do not reflect the actual reaction yields.



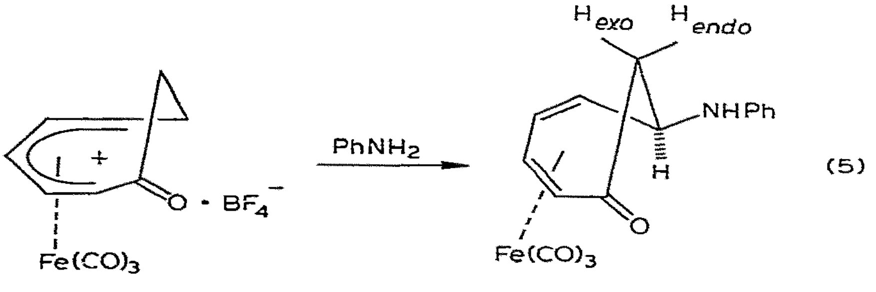
(4)

The structure of the above products (vide infra) are presented in eq. 4. The anilino alcohol complex IX was obtained independently by the chemical reduction of VIII (Zn/HAc) followed by complexation with $Fe_2(CO)_9$, thus confirming the gross structure IX. The *cis* configuration of the PhNH and OH groups follows from the chemical reduction of the $\geq$N—O bond and also from NMR evidence (vide infra). From our analysis of the previous systems it is apparent that the complexed cycloheptadiene ring system adopts the *exo* conformation, i.e., the CH_2 and the metal groups are situated at the opposite faces of the diene plane. Although the diene may not necessarily be completely planar, models reveal that the non-bonded interactions of the "axial" C(1) and C(6) substituent with an *endo* metal group (see structure IX) are considerably smaller than those of the latter group with the CH_2 group in an *exo* conformation. Being in a *cis* configuration, the NHPh and OH groups in IX were assigned an *endo* configuration on the basis of the following NMR evidence. The signals of H(2) and H(5) (multiplets) at δ 3.08 and 3.28 ppm collapsed into two doublets (J 5.0 Hz) upon irradiation of the H(3) and H(4) signals. The above coupling constant is taken requiring a dihedral angle different from 90° between H(1) and H(2) and also H(5) and H(6). Such a requirement is accommodated by structure IX, where H(1) and H(6) are assigned the *exo* configuration, involving a dihedral angle of ~0°. It follows that the NHPh and OH group at C(1) and C(6) in IX must have the *cis-endo* configuration.

Finally it should be noted that since the reaction of the anilino alcohol, obtained by the chemical reduction of VIII, with $Fe_2(CO)_9$ gave only complex IX, the latter is not a reaction intermediate for any of the other products of reaction 4. A similar conclusion was also reached for the previous system (eq. 1).

The bicyclic lactone X was characterized by mass spectra and elemental analysis. An IR band at 1695 cm^{-1} was assigned to the lactam CO group, while no NH stretching band could be detected. A detailed analysis of the spin-decoupled NMR spectrum of X supports our structural assignment.

The structure of *cis*-6-anilino-cyclohepta-2,4-diene-1-oneiron tricarbonyl (XI) was assigned to a substance possessing both NH and C=O IR stretching bands. Both elemental analysis and mass spectral data conform with correct molecular formulae. The *exo* isomer XIV was prepared by treating the cycloheptadienylium keto cation XIII with aniline; in this reaction the nucleophile attacks the *trans* face of the ring (eq. 5) [5]. The NMR spectra with detailed line assignments for both isomers, are depicted in Fig. 2. Again a reasonable planarity of the dienone system is achieved when C(7) projects from the average plane of the ring. All the line assignments were generated by spin-decoupling experiments. The spectra exhibit several important features which can be exploited for stereochemical assignments. The multiplicity of the H(5) proton in XI and XIV reflects the



(5)

(XIII) (XIV)

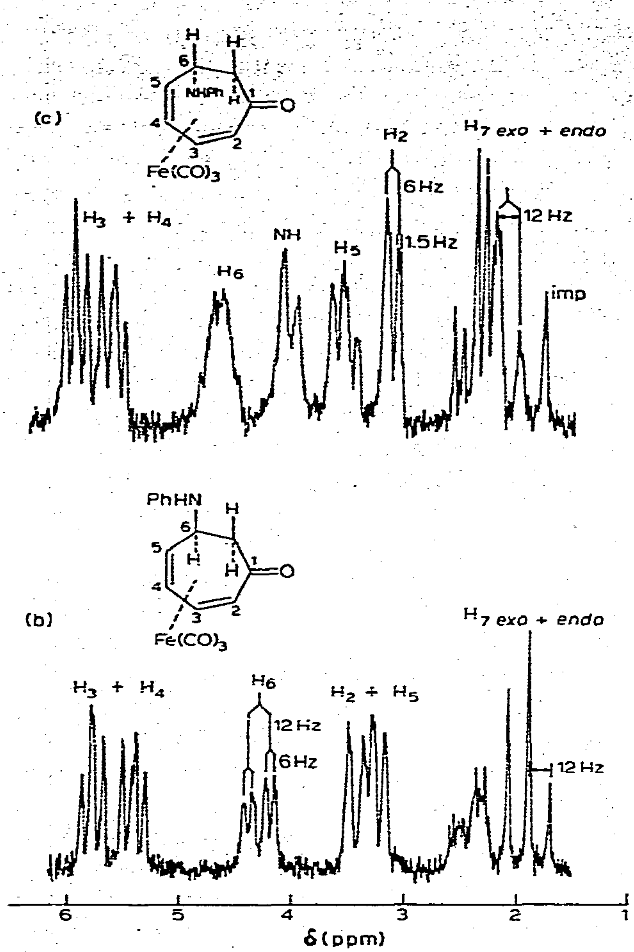
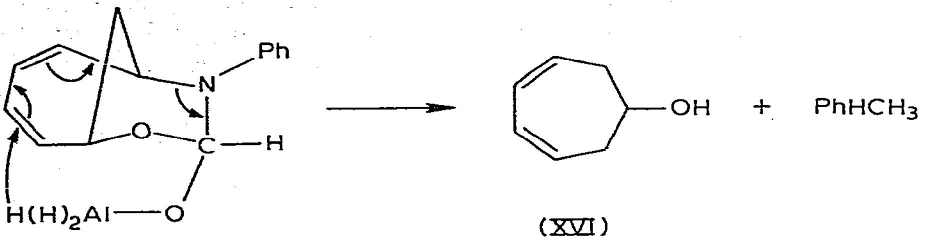


Fig. 2. NMR spectra at 60 MHz in $CDCl_3$ (TMS internal reference) of (a) XI and (b) XIV. Aromatic signals are omitted.

stereochemistry at C(6). While the signal of H(5) in XIV is a doublet ($J_{5,4}$ 5 Hz; $J_{5,6}$ 0 Hz), in XI it exhibits a four-line system which gives rise to an apparent triplet ($J_{5,4} \cong J_{5,6} = 5$ Hz). This is taken as evidence that the anilino group in XIV possesses the *exo* configuration, thus allowing for a dihedral angle of 90° between H(5) and H(6). The *endo* configuration of the anilino group in XI follows from this argument. Supporting evidence for such an assignment was adduced by analyzing the high field signals of the H(7) protons which give rise to an ABX spin system, with J_{AB} 12 Hz in both XI and XIV. Appropriately, only XIV which possesses a *trans-anti* planar arrangement of the *exo*-H(7) and H(6) exhibits an additional large spin coupling (J 12 Hz), as reflected by the apparent triplet (doublet of doublets) at highest magnetic field (Fig. 2).

The predominant component (31%) of reaction 4 is the carbamate XII. It separates out during the reaction in benzene, and was isolated uncomplexed. All analytical and spectral data support the structure assigned to this product. Its IR spectrum exhibits a C=O stretching band and 1685 cm^{-1}, while all the protons were accounted for and identified by double irradiation experiments (see experimental section). Reduction of XIV with $LiAlH_4$ gave 3,5-cycloheptadiene-1-ol (XVI) and *N*-methylaniline, both identified by comparison with authentic samples. These products can be rationalized in terms of hydrogenolysis of the allylic amino group with concomitant migration of the diene system (eq. 6).



(XV) (XVI) (6)

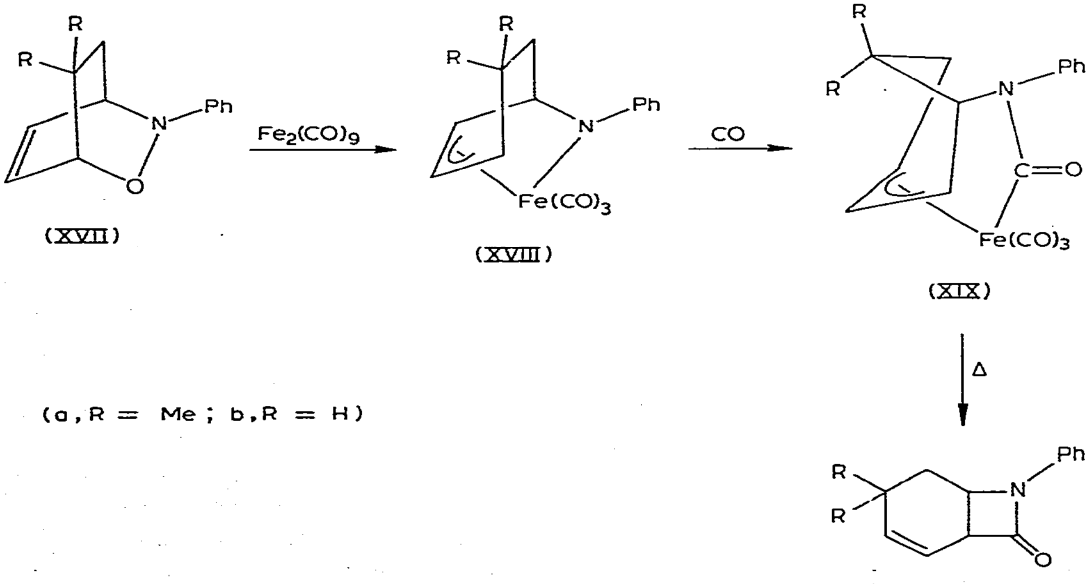
Discussion

The unique structural features of the two anilinocycloheptadiene complexes III and IV (eq. 1) are the absence of the original oxygen atom present in the starting materials I, and their *endo* configuration.

The mechanism of the formation of the stable products III and IV from I is of interest, as it may provide ideas for further work. At present, some of the mechanistic proposals must be speculative.

We previously described [4] the interception of a reactive σ—π-allyl intermediate XIXa (Scheme 1), the structure of which was determined by X-ray crys-

SCHEME 1.



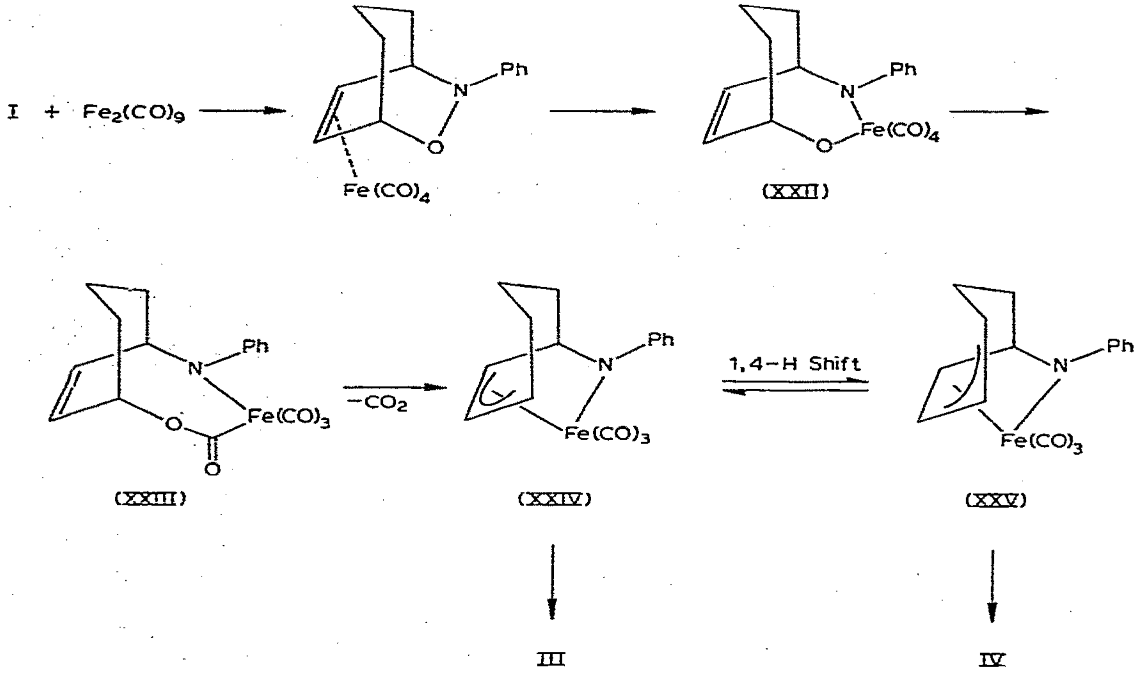
(XVII) (XVIII) (XIX) (XX)

(a, R = Me; b, R = H)

tallography. In a thermal reaction XIXa produced XXa. Compound XVIIb produced XXb directly, while intermediate XIXb could not be isolated. Along with XXb there was isolated *endo*-5-anilinocyclohexa-1,4-dieneiron tricarbonyl (XXI). Based on these and other observations, we proposed that XVIII is the precursor for XIX. Recently, a σ—π-allyl system similar to XVIII was generated by irradiation of *N*-carbomethoxyvinylaziridine and $Fe(CO)_5$ [7]. Such a compound was found to be stable and to undergo reversible insertion of CO into the σ-Fe—N$<$ bond. We have therefore proposed that central to the reaction of the $>$N—O bond with $Fe_2(CO)_9$ is the primary oxidative insertion of iron carbonyl into this rather weak bond. From this point, several competing reactions may take place, depending on the molecular structure.

When applied to I, the mechanistic pattern described leads to Scheme 2. The

SCHEME 2.

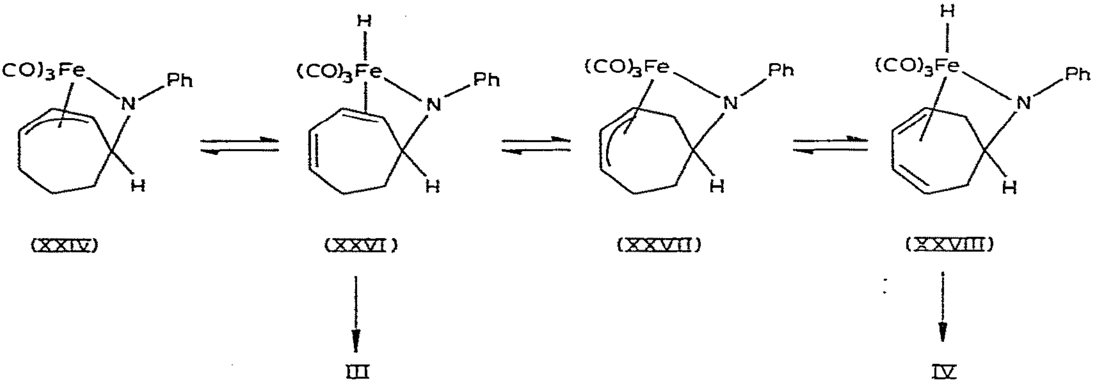


final intermediate XXIV is presumed to be produced via XXII and XXIII. Two experimental results support the formation of XXIII: (a) In all reactions of this type the CO_2 which is evolved incorporates the orginal oxygen atom. (b) In some systems carbamates are produced. Intermediate XXIII is a logical precursor for the formation of such a functional group by elimination of $Fe(CO)_3$. That no carbamate was produced from I may merely imply that the rate of the competing CO_2 elimination is faster.

While XXIV satisfactorally accounts for III, we must invoke XXV to account for the isomeric diene IV. The direct isomerization III ⇌ IV was excluded inasmuch as the reaction of VII with $Fe_2(CO)_9$ led to the formation of all three complexes (eq. 3), none of which underwent thermal interconversion under the original reaction conditions. Dieneiron tricarbonyl complexes do isomerize, however, under more drastic condition [8]. It is therefore concluded that III and IV are kinetically controlled products. Formally the transformation XXIV $\rightleftharpoons$ XXV involves a 1,4-H shift. Although such a suprafacial shift is disallowed (assuming a 3-electron π-allyl system in the ground state), back donation from iron to ψ_3 of the allyl system may facilitate such a sigmatropic shift [9]. In this connection we note that we were able to demonstrate such a 1,4-H shift in a similar complexed π-allyl system through a labelling experiment [2].

Alternatively and perhaps more attractive is the following mechanistic proposition. Since both the isomerization of XXIV → XXV and the formation of the dienes III and IV requires the cleavage of an allylic C—H bond, we shall attempt to describe these two reactions by a combined mechanism (Scheme 3).

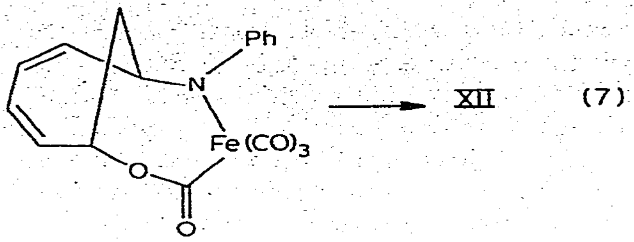
SCHEME 3.



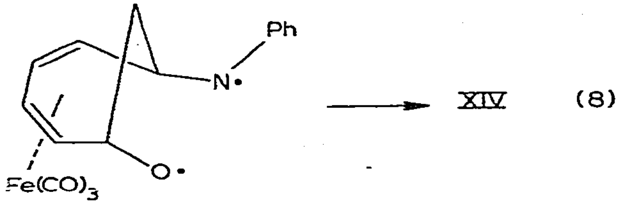
It is proposed that the exchange between the four species XXIV, XXVI, XXVII and XXVIII takes place via the hydrido complexes XXVI and XXVIII, which may donate the H atom to either end of the diene system. The irreversible reductive elimination of the latter two complexes leads to the final products III and IV, respectively (see Scheme 3). Such a rearrangement may conceivably occur also in XVIIIb (Scheme 1), but since it would give a product identical to the final diene product XXIb, it cannot be detected.

The behaviour of VIII toward $Fe_2(CO)_9$ differs from that of I inasmuch as on the one hand no anilinotriene complex could be isolated, and on the other hand substantial quantity (31%) of the carbamate XII was produced along with small quantities (0.5—2%) of X and XI. It was again demonstrated that neither the free nor the complexed anilino alcohol (IX) serve as intermediates for the formation of the rest of the products (eq. 4). The carbamate XII is insoluble in the reaction solvent, and precipitates out upon formation, and is therefore not complexed. It is noteworthy that the reaction of the $\geqslant$N—O bond in VIII with $Fe_2(CO)_9$ is faster than complexation of the diene system.

Intermediate XXIX (eq. 7), which is analogous to XXIII, is suggested as the precursor for the carbamate XII. The formation of small quantity of the lactam X, can be rationalized by assuming the loss of CO_2 from XXIX, in much the same way as XX is formed from XVII, i.e. via an intermediate of type XIX. Apparently, the formation of carbamate is much faster than the loss of CO_2 from XXIX.



(XXIX)



(XXX)

Lactams such as X have been previously encountered by us [4]. They are produced via σ—π-allyl intermediates viz. XVIII (Scheme 1) which was actually isolated and was transformed in a thermal reaction to a lactam such as XX. It is logical to assume that a similar intermediate is also the precursor for X.

The dienone XI, although encountered in minute quantity, is important inasmuch as this type of product has not been encountered previously. It is tempting to invoke the biradical XXX as the precursor, which by H transfer from C to N generates the stable dienone XI. This is a well-known photochemical reaction [10], which may be thermally allowed due to the close interaction of the complexed metal with the $\geq$N—O bond in XXX.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on Perkin—Elmer Spectrophotometers models 337 and 257. NMR spectra were measured with Jeol JNM-C-60 HL and Varian HA-100 with TMS as internal reference standard. Mass spectra were obtained with the following instruments: Atlas CH4, Perkin—Elmer—Hitachi RMU-6 and Du Pont 21-491B, using direct inlet systems and ionization potential of 60 eV. Nitrogen was purified on a W/Cu column at 300°C and then dried.

N-Phenyl-2-oxa-3-azabicyclo[2.2.3]nona-8-ene (I)

A solution of 1,2-cycloheptadiene (7.5 g) and nitrosobenzene (5 g) in ether (100 ml) was kept at 3°C for 3 days. The residue after evaporation was chromatographed on neutral alumina. A solution of CH_2Cl_2/petroleum ether eluted a crystalline substance, (I, 6 g, m.p. 58—59°C, after crystallisation from pentane). Analysis: Found: C, 77.2; H, 7.41. $C_{13}H_{15}NO$ calcd.: C, 77.6; H, 7.46%. NMR spectrum ($CDCl_3$): δ (ppm) 7.0 (m, 5 H); 6.0 (m, 2 H).

Reaction of I with $Fe_2(CO)_9$

A solution of I (2 g; 10 mmol) in dry benzene (40 ml) and $Fe_2(CO)_9$ (8.85 g; 25 mmol) was stirred under nitrogen at 50°C for 1 h. The residue after evaporation was chromatographed on basic alumina. Methylene chloride/petroleum ether (1/9) eluted a pale yellow solid, III (22%), m.p. 118—119°C (benzene/petroleum ether). Analysis: Found: C, 58.99; H, 4.59; N, 4.89. $C_{16}H_{15}FeNO_3$ calcd.: C, 59.10; H, 4.62; N, 4.31%. Mass spectrum: *m/e* 325(M^+), 297 (M^+ — CO), 269(M^+ — 2 CO), 241(M^+ — 3 CO), 148(241 — $PhNH_2$). Infrared spectrum: ($CDCl_3$): 3420 (NH) cm^{-1}; (hexane): 2040, 1985, 1980 (C≡O) cm^{-1}. NMR spectrum, see Fig. 1c.

Further washing with 15% CH_2Cl_2/petroleum ether resulted in a yellow solid, (IV, 16%, m.p. 153—154°C, needles from pentene). Analysis: Found: C, 59.22; H, 4.66; N, 5.6. $C_{16}H_{15}FeNO_3$ calcd.: C, 59.10; H, 4.62; N, 4.31%. Mass spectrum: *m/e* 325(M^+), 297(M^+ — CO), 269(M^+ — 2 CO), 241(M^+ — 3 CO). Infrared spectrum ($CHCl_3$): 3420 (NH) cm^{-1}; (hexane): 2043, 1981 (C≡O) cm^{-1}. NMR spectrum: see Fig. 1a.

Further elution with CH_2Cl_2 gave II (30%, m.p. 94—95°C, ethyl acetate/petroleum ether). Mass spectrum: *m/e* 203(M^+, $C_{13}H_{17}NO$). Infrared spectrum ($CHCl_3$): 3520 (OH free), 3370 (NH), 1600, 1500 (Ph) cm^{-1}. NMR spectrum ($CDCl_3$): δ (ppm) 7.15 (m, 2 H), 6.62 (m, 3 H), 5.7 (m, 2 H), 4.4 (m, 1 H), 4.0 (s, 2 H), 3.95 (m, 1 H), 1.75 (m, 6 H).

An identical substance was obtained by reducing I with Zn in HAc.

exo-5-Anilinocyclohepta-1,3-dieneiron tricarbonyl (VI)

Cycloheptadienyliumiron tricarbonyl tetrafluoroborate [5] was treated with aniline in methylene chloride, m.p. 88—89°C (hexane). Mass spectrum: *m/e* 325(M^+, $C_{16}H_{15}FeNO_3$), 297(M^+ — CO), 269(M^+ — 2 CO), 241(M^+ — 3 CO). Infrared spectrum ($CHCl_3$): 3390 (NH) cm^{-1}; (hexane): 2045, 1970 (C≡O) cm^{-1}. NMR spectrum Fig. 1b.

5-Anilino-1,3-cycloheptadiene (VII)

Compound III (1.9 g) in dry acetone (30 ml) was stirred with trimethylamine oxide at room temperature for 12 h [6]. The residue after filtration and evaporation of the solvent, was chromatographed on basic alumina, to give an oil (VII, 84%). Mass spectrum: *m/e* 185(M^+, $C_{13}H_{15}N$). Infrared spectrum ($CHCl_3$) 3420 (NH) cm^{-1}. NMR spectrum ($CDCl_3$: δ (ppm) 7.18 (m, 2 H), 6.67 (m, 3 H), 5.86 (m, 4 H), 4.20 (m, 1 H), 3.55 ((br), s, NH), 2.80—1.50 (m, 4 H).

A sample of the above was treated with 4-phenyl-1,2,4-triazolin-3,5-dione to give colourless crystals of the adduct, m.p. 215°C (dec.) (from ethanol). Analysis: Found: C, 69.62; H, 5.62. $C_{21}H_{20}N_4O_2$ calcd.: C, 69.90; H, 5.56%.

When IV was treated as above, the product (oil) gave a TLC spot with an R_f different from that of VII.

Reaction of 5-anilino-1,3-cycloheptadiene with $Fe_2(CO)_9$

A solution of VII (0.985 g; 5.3 mmol), in hexane (30 ml) and $Fe_2(CO)_9$ (9.5 g 26 mmol), was stirred under nitrogen at 50°C for 2 h. The residue after filtration and evaporation of the solvent was chromatographed on neutral alumina. Petroleum ether eluted III, 0.855 g (49.5%). A mixture of the isomers IV and

VI was eluted with 15% CH_2Cl_2 petroleum ether. The identity of these substances was determined by TLC and NMR. The composition of the mixture was determined from the NMR integration; IV (13%), VI (18%).

Reaction of 8-phenyl-7-oxa-8-azabicyclo[4.2.1]nona-2,4-diene (VIII) with $Fe_2(CO)_9$

A solution of VIII [11] (2 g; 10 mmol) in dry benzene (40 ml) and $Fe_2(CO)_9$ (4 g; 11 mmol) was stirred under nitrogen at 48 for 1 h.

9-Phenyl-7-oxa-9-azabicyclo[4.3.1]deca-2,4-diene-8-one (XII)

Following filtration and partial removal of the solvent, a crystalline substance separated XII (31%), m.p. 170—172°C (ethyl acetate). Analysis: Found: C, 73.80; H, 5.74; N, 6.01. $C_{14}H_{13}NO_2$ calcd.: C, 73.95; H, 5.73; N, 6.16%. Mass spectrum: *m/e* 227(M^+), 183($M^+ - CO_2$). Infrared spectrum ($CHCl_3$): 1685 (C=O) cm^{-1}. NMR spectrum ($CDCl_3$): δ (ppm) 7.26 (m, 5 H), 5.98 (m, 4 H), 5.03 (m, 1 H), 4.54 (t, 1 H), 2.96 (ddd, *J* 15.7 and 4.5 Hz, 1 H), 2.30 (dt, *J* 15 and 1 Hz, 1 H).

The carbamate XII (0.152 g) was reduced with $LiAlH_4$ (0.057 g) in ether (9 ml). After a 24 h reflux the mixture was decomposed in the usual manner. The oil was chromatographed on basic alumina. A solution of 40% CH_2Cl_2/petroleum ether eluted *N*-methylaniline (15 mg) identified by TLC and NMR spectrum. Further elution gave 3,5-cycloheptadienol (XVI), identical with the reduction product of tropone with $LiAlH_4$ [12].

8-Phenyl-8-azabicyclo[4.2.1]nona-2,4-diene-7-one (X)

The filtrate from XII was reduced to a small volume and chromatographed on basic alumina. A mixture of CH_2Cl_2/petroleum ether (1/4) eluted an oil which was a mixture. It was separated by preparative TLC (silica) with benzene as the developing solvent. The most polar compound was obtained as yellow needles (X, 0.5%, m.p. 155°C (dec)). Mass spectrum: *m/e* 350(M^+; $C_{17}H_{13}FeNO_4$), 322($M^+ - CO$), 294($M^+ - 2\ CO$); 266($M^+ - 3\ CO$). Infrared spectrum ($CHCl_3$): 1695 (C=O) cm^{-1}; (hexane): 2050, 2000, 1970 (C≡O) cm^{-1}. NMR spectrum ($CDCl_3$): δ (ppm) 7.36 (m, 5 H), 5.58 (ddd, *J* 5.5, 3.5 and 2 Hz, 1 H), 5.48 (ddd, *J* 5, 4 and 1 Hz, 1 H), 4.15 (dt, *J* 6, 2 and 1 Hz, 1 H), 3.50 (t, 1 H), 3.25 (t, 1 H), 3.0 (dd, *J* 4 and 2.5 Hz, 1 H), 1.76 (m, 2 H). This compound was followed by an additional component which could not be purified or identified.

endo-6-Anilinocyclohepta-2,4-diene-1-one (XI)

The original chromatographic column was further developed with methylene chloride/petroleum ether (1/1). There was obtained an oil, which following re-chromatography (basic alumina; 30% CH_2Cl_2/petroleum ether) gave XI, (2%), yellow needles, m.p. 151—152°C (hexane). Mass spectrum: *m/e* 339(M^+, $C_{16}H_{13}FeNO_4$), 311($M^+ - CO$), 283($M^+ - 2\ CO$), 255($M^+ - 3\ CO$). Infrared spectrum ($CHCl_3$) 3418 (NH), 1655 (CO) cm^{-1}; (hexane): 2000, 2060 (C≡O) cm^{-1}. NMR spectrum: see Fig. 2a.

exo-6-Anilinocyclohepta-2,4-diene-1-olyliron tricarbonyl (IX)

Further development of the column with CH_2Cl_2/petroleum ether (1/1) gave

IX (4%), yellow crystals, m.p. 90—92°C (ethyl acetate/hexane). Mass spectrum: *m/e* 341(M^+, $C_{16}H_{15}FeNO_4$), 313(M^+ — CO), 285(M^+ — 2 CO), 257(M^+ — 3 CO). Infrared spectrum ($CHCl_3$): 3590 (OH), 3420 (NH) cm^{-1}; (hexane): 2026, 1995, 1985 (C≡O) cm^{-1}. NMR spectrum ($CDCl_3$): δ (ppm) 7.14 (q, 2 H), 6.65 (m, 3 H), 5.35 (m, 2 H), 4.74 (m, 2 H), 4.13 (m, 1 H), 3.85 (m, 1 H), 3.28 (m, 1 H), 3.08 (m, 1 H), 1.60 (m, 2 H).

An authentic sample of IX was prepared by treating *cis* -6-anilinocyclohepta-2,4-diene-1-ol [13] (0.6 g; 3.2 mmol) in dry benzene (30 ml) with $Fe_2(CO)_9$ (1.75 g; 4.8 mmol) under nitrogen at 40°C for 10 h. Chromatography gave 0.158 g, m.p. 90—92°C (ethyl acetate/hexane), identical with IX. Analysis: Found: C, 56.37, H, 5.02, N, 4.33. $C_{16}H_{15}FeNO_4$ calcd.: C, 56.10; H, 4.40; N, 4.40%.

exo-6-Anilinocyclohepta-2,4-diene-1-oneiron tricarbonyl (XIV)

Cycloheptadien-1-onyliumiron tricarbonyl tetrafluoroborate [14] (XIII) was treated with aniline in methylene chloride, yellow needles, m.p. 138—140°C (hexane). Mass spectrum: *m/e* 339(M^+, $C_{16}H_{16}FeNO_4$). 311(M^+ — CO), 283(M^+ — 2 CO), 255(M^+ — 3 CO). Infrared spectrum ($CHCl_3$); 3400 (NH), 1650 (C=O) cm^{-1}; (hexane): 2000, 2008, 2070 (C≡O) cm^{-1}. NMR spectrum: see Fig. 2b.

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