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# REACTION OF TRANSITION METAL CARBONYL WITH HETEROCYCLIC SYSTEMS—IV

## THE REACTION OF $Fe_2(CO)_9$ WITH 3-PHENYL-2-OXA-3-AZA-[2.2.2]OCT-5-ENE

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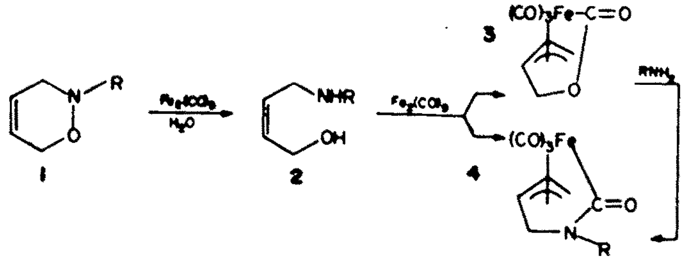
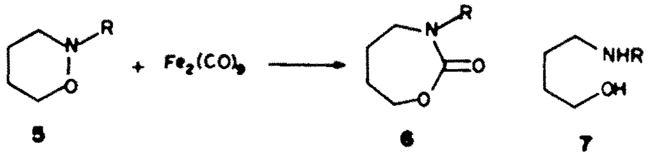
**Abstract**—The structure of the products from the titled reaction were determined. The most interesting ones are 11 and 12 which lack the original oxygen atom present in the starting material (8). In an attempt to probe the mechanism of the reaction, the reactivity of the dialkyl derivatives 15 and 16 toward $Fe_2(CO)_9$ was studied. An intermediate complex was isolated from the reaction of 16 with $Fe_2(CO)_9$. Its structure was determined by X-ray crystallography (Fig. 2). A reaction sequence was proposed and depicted in Scheme 1.

In our previous reports[1a–c] of this series we have uncovered the reactivity of the >N–O– bond toward $Fe_2(CO)_9$ under mild reaction conditions. Two types of reactions were discerned:

(a) Elimination of one hetero-atom from 1 and formation of either the $\sigma$–$\pi$-allyl lactone (3) or lactam (4), depending on the substituent R (eqn 1). It was demonstrated that the process is a two-steps reaction with the initial reduction of the >N–O– bond of 1 to the corresponding amino-alcohol (2), which in a second reaction with $Fe_2(CO)_9$ yields the final products.[1b] The benzene must therefore be moist.



(1)



(2)

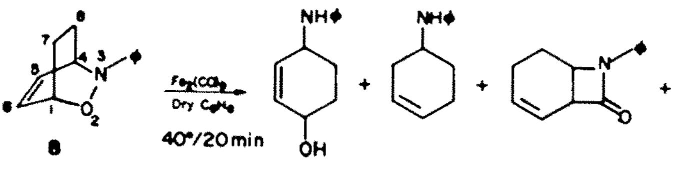
The lactone 3 could be readily converted to the lactam 4 using an amine and $Al_2O_3$ catalysis.[1c] Proper labelling experiments have unequivocally established an $S_N2'$ type reaction, inasmuch as the amine attacks the terminal carbon of the $\pi$-allyl system of 3.[1c]

(b) A novel insertion reaction of CO to the >N–O– bond,[1b] when 5 was reacted with $Fe_2(CO)_9$, the tetramethylene carbamate 6 was isolated in fair yield (eqn 2). The same insertion reaction occurs also when acyclic tri-substituted hydroxyl amines are exposed to $Fe_2(CO)_9$.[2] Invariably the cyclic carbamate was accompanied by the amino-alcohol 7, most probably due to traces of water present in the reaction system. When $R_1ONR_2$ was used, the carbamate $R_1OCONR_2$ was accompanied by the reduction products $R_1OH$ and $R_2NH$.[2]

In the present work we have extended the investigation by examining the reactivity of the >N–O– bond toward $Fe_2(CO)_9$ in 3-phenyl-2-oxa-3-aza-[2.2.2]oct-5-ene (8) and related alkyl derivatives of 8. The interception of a complexed intermediate and its unambiguous X-ray structure determination, enabled us to probe into the mechanism of the reaction.

### RESULTS AND DISCUSSION

In a previous communication,[1a] we have described the products which were isolated from the reaction of 8 with $Fe_2(CO)_9$ (eqn 3). Although structurally similar, the oxazines (1 and 8) react differently with $Fe_2(CO)_9$ as can be judged from the different types of products generated by these two reactions (compare eqns 1 and 3). We recall that the amino alcohol 2 is an intermediate in the formation of 3.[1b] The analogous amino alcohol (9) was also isolated in reaction 3; however, in contrast to the pre-



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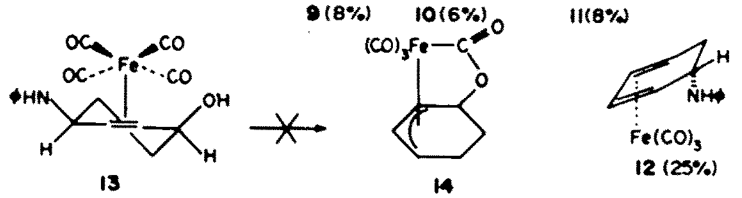

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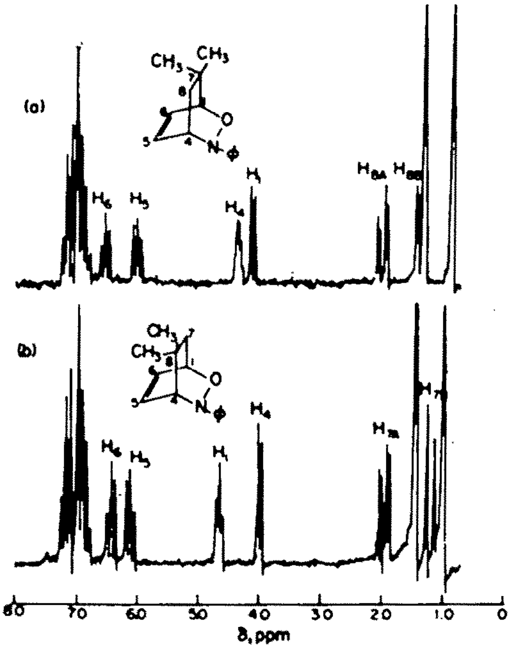


Fig. 1. NMR spectra in $CDCl_3$ (100 MHz). (a) 16; (b) 15.

vious reaction, it was totally inert toward $Fe_2(CO)_9$ and was recovered unchanged from the mixture. By analogy with the reactivity of the amino alcohol (2) toward $Fe_2(CO)_9$, we have anticipated the formation of 14, via the intermediate 13,[3] which is a known and stable compound.[4] Inasmuch as 9 was unreactive toward $Fe_2(CO)_9$ we conclude that *cyclic* monoene intermediates such as 13 either does not form at all or is unreactive. It can be argued that the pseudo equatorial pseudo axial conformations of the OH and NHϕ groups generate longer non-bonding distances between these groups and the iron carbonyl in 13, thus preventing effective interaction which is necessary in this reaction. In fact this case is analogous to the known unreactivity of 3-bromocyclohexene toward $Fe_2(CO)_9$ at variance of the reactivity of allyl halides in the same reaction.[5]

The amino-alcohol (9) must therefore be produced in a reduction reaction due to the presence of traces of water, and it does not participate further in any other reactions. We turn now to examine some of the mechanistic aspects of the reactions which generate compounds 10, 11 and 12, all of which lack the original oxygen atom present in 8. We have elaborated on the molecular structure of the diene 12 in the first communication. The *endo* configuration of 12 was supported by spectral data[1a] and by the synthesis of the *exo* isomer from cyclohexadienylium iron tricarbonyl tetrafluoroborate and aniline.[1a] From a structural point of view the diene complex 12, which is the major product, represents a formal scission of the $\rangle$N–O– bond and elimination of O and H atoms. The logical source of this H atom is either the $CH_2$– (8) or $CH_2$– (7) group in compound 8. Since the overall transformation is most probably a stepwise sequence, we sought to block the step which involves the abstraction of the H atom in 8. Such an approach should:

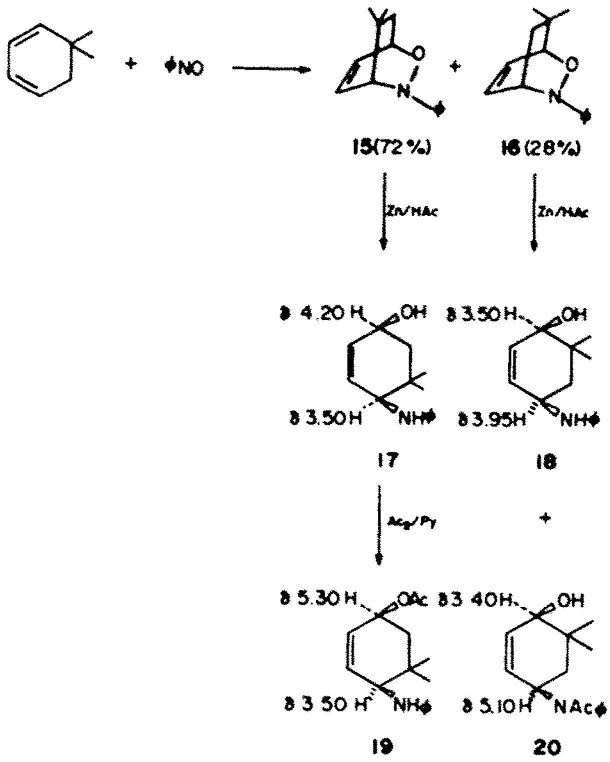
(a) reveal the identity of a H atom which migrates to nitrogen;

(b) divert the reaction to other available pathways;

(c) create a situation where an intermediate could possibly be trapped.

To attain the above-mentioned goal we have prepared the isomeric *gem*-dimethyl derivatives (15 and 16) which were separated from the reaction mixture of 6,6-dimethyl-1,3-cyclohexadiene and nitrosobenzene (eqn 5). The structural assignments of these two compounds were hampered by unexpected features in their NMR spectra (Fig. 1). We have planned to exploit the relationship between the multiplicity and the chemical shift of the signals of the two bridge protons of 15 and 16, in order to differentiate between the two isomers. It is clear (Fig. 1a, b) that in *both spectra* the signal of the low multiplicity (Hα to $CMe_2$) resonates at high field with respect to the signal of the high multiplicity (Hβ to $CMe_2$). Since the NMR results turned out to be ambiguous, the following scheme was executed. Each of the isomers was reduced (Zn/HAc) to the corresponding anilino alcohol (eqn 5) which was then mono-acetylated.

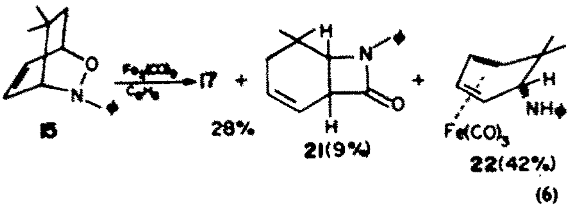
The major component of the cycloaddition was assigned structure 15 on the basis of the following observations. Its reduction product (17) exhibited an NMR spectrum similar to that of the parent bicyclic precursor. Upon acetylation of 17, a mono-acetate (19) was isolated. Its IR stretching bands at 1730 (ester CO) and 3420 $cm^{-1}$ (NH) were taken as evidence for O rather than N acetylation. It was the *high multiplicity* NMR signal of 17 which was shifted downfield ($\Delta\delta = 1.1$ ppm) in 19 upon O-acetylation. Therefore, the *gem*-dimethyl group in 19, 17 and 15 must reside β to the nitrogen. It follows that structure 16 must be assigned to the other, minor component. This was verified by a similar procedure. The mono-N-acetyl (20) was isolated directly from the reaction mixture (Zn/HAc), exhibiting IR stretching bands at 1650 (amide CO) and 3570 $cm^{-1}$ (OH). Again, it was the NMR signal of the high multiplicity in 18 which shifted downfield upon acetylation ($\Delta\delta = 1.15$ ppm), thus



(5)

confirming structure 16 for the minor component of the cyclo-addition reaction (eqn 5).

We then subjected each of the isomeric oxazines to the action of $Fe_2(CO)_9$. The results (*vide infra*) of such a reaction with 15 are described in eqn (6).

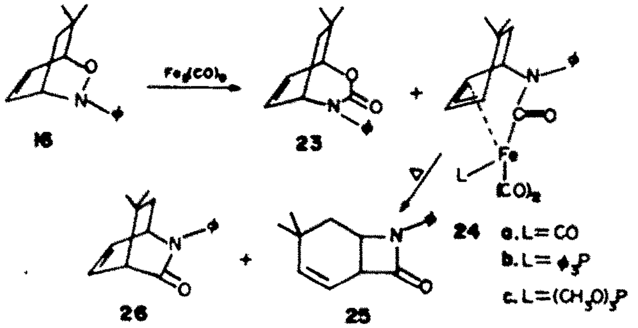


(6)

The nature and the gross distribution of the products are essentially equivalent to those of the unsubstituted system (eqn 3). The structure of 21 and 22, which are the dimethyl analogs of 11 and 12 respectively, was determined from analytical and spectral data (Table 1), in conjunction with the previous data for 11 and 12.[1a] The *endo* configuration of 22 was inferred from the chemical shift of H-5 (δ 3.40) which is similar to that recorded for the corresponding proton of 12 (δ 3.60), where the stereochemistry was unequivocally determined.[1a] The coupling constants of the bridge protons (5.0 Hz) in 21 was taken as evidence[6] for a *cis* ring junction, which was also in accordance with the stereochemistry of 11.[1a] These results, and specifically the formation of the diene complex (22) point out that it is the H atom β to the oxygen (H-(7); structure 8) which is eliminated in the reaction with $Fe_2(CO)_9$, and no skeletal rearrangement takes place.

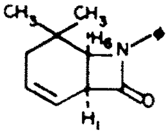
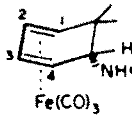
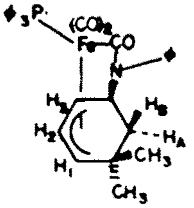
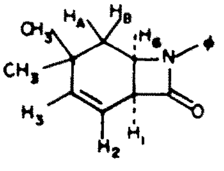
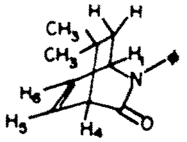
The reaction of the isomeric 16 with $Fe_2(CO)_9$ (eqn 7) was strikingly different from that of 15 (eqn 6). Three metal-free organic compounds were formed in low yields. The cyclic carbamate 23 was actually isolated from the mixture and its structure was determined (Experimental). It was demonstrated (tlc, IR) that the mixture also contains 25 and 26. Due to technical difficulties we did not pursue their isolation at this stage. Later, we shall elaborate on the identity of these two compounds.

The major product (30%) of this reaction (eqn 7) is a labile organometallic complex, which was isolated by rapid chromatography at 0°. Structure 24a was assigned (*vide infra*) to this compound. The presence of the



(7)

Table 1. NMR* and IR data

| Compound | δ(ppm) | | Multiplicity | J(Hz) | νmax(cm$^{-1}$) |
|---|---|---|---|---|---|
| <br>**21** | $CH_3$ | 0.98, 1.04 | s, s | | |
| | $H_{4A,B}$ | 1.79, 2.11 | dq | $J_{AB} = 16.0$ | 1745 |
| | $H_1$ | 3.76 | m | $J_{12} = 5.0; J_{13} = 2.0$ | (C=O) in |
| | $H_6$ | 4.07 | dd | $J_{61} \sim 5.0; J_{62} = 2.0$ | $CHCl_3$ |
| | $H_{2,3}$ | 5.90 | m | | |
| | $\phi$ | 7.2 | m | | |
| <br>**22** | CH | 1.00, 1.10 | s, s | | |
| | $H_1$ | 2.83 | dd | $J_{12} = 6.0; J_{13} = 2.0$ | 3425 |
| | $H_4$ | 3.01 | ddd | $J_{43} = 6.0; J_{42} = 2.0$ | (N–H) in $CHCl_3$ |
| | $H_5$ | 3.40 | br.s.$^b$ | $J_{54} = 2.5$ | 2040, |
| | NH | 3.74 | m | | 1985, |
| | $H_{2,3}$ | 5.25 | m | | 1980 ($C\equiv O$) in |
| | $\phi$ | 6.43–7.22 | m | | hexane |
| <br>**24b** | $CH_3$ | 0.92, 1.23 | s, s | | 1555 |
| | $H_{5A,B}$ | 0.94, 1.33 | q | $J_{AB} = 14.0$ | (NCOFe) in |
| | $H_1$ | 2.84 | dd | $J_{12} = 6.0; J_{13} \simeq 1.0$ | $CHCl_3$ |
| | $H_4$ | 4.24 | m | | 2015, |
| | $H_2$ | 4.60 | dt | $J_{2P} = 18.0; J_{23} = 5.5$ | 1965 |
| | $H_3$ | 5.24 | ddd | $J_{34} = 7.5$ | ($C\equiv O$) in |
| | $\phi$ | 7.35 | m | | hexane |
| <br>**25** | $CH_3$ | 0.96, 1.03 | s, s | | |
| | $H_{5AB}$ | 1.89, 1.80 | dq | $J_{AB} = 14.0$ | 1735 |
| | $H_1$ | 3.76 | dd | $J_{16} = 5.0; J_{12} = 2.0$ | (C=O) in |
| | $H_6$ | 4.46 | q | $J_{6,5A} = 4.0; J_{6,5B} = 5.0$ | $CHCl_3$ |
| | $H_{2,3}$ | 5.78 | br.s. | | |
| | $\phi$ | 7.25 | m | | |
| <br>**26** | $CH_3$ | 1.03, 1.23 | s, s | | |
| | $H_{7AB}$ | 1.95, 1.45 | dq | $J_{AB} = 13.0$ | 1670 |
| | $H_4$ | 3.14 | dd | $J_{45} = 6.0; J_{46} = 2.5$ | (C=O) in |
| | $H_1$ | 4.62 | m | $J_{1,7A} = 3.7; J_{1,7B} = 2.0$ | $CHCl_3$ |
| | $H_{5,6}$ | 6.52 | m | | |
| | $\phi$ | 7.30 | m | | |

*Measured in $CDCl_3$(TMS) on a 100 MHz instrument. $^b$Doublet after the addition of $D_2O$.

$>NCOFe(CO)_3$– structural unit was inferred from the IR band at 1575 cm$^{-1}$ and the three bands at the 2000 cm$^{-1}$ region.

Aside from small shifts and minor changes in the coupling constants, the NMR spectra of **16** and **24a** were quite similar. It was, however, ascertained (integration) that **16** and **24a** possess the same number of H atoms. Elemental analysis and mass spectra of **24a** were uninformative due to the thermal instability of the compound under investigation. Improved stabilization of the complex **24a** was achieved by transforming it to the triphenylphosphine complex **24b**. The IR spectrum of **24b** exhibits now only two $C\equiv O$ stretching bands and the frequency of the $>NCOFe$ band was lowered by 20 cm$^{-1}$. Such a shift is consistent with the stronger σ donation of the P atom. Although more stable, the mass spectrum of **24b** exhibits only fragmentation peaks. Carbon analysis was low by 1.2% and could equally well fit a molecular formula with one additional O atom as was previously postulated by us.[1a] The NMR spectrum of **24b** was drastically affected by the triphenylphosphine substitution. All the signals were now chemically shifted (Table 1), and only the central H atom of the π-allyl system was coupled with the P atom ($J = 18.0$ Hz); similar behavior was previously encountered.[7]

Since our mechanistic study hinges upon the above intermediate complex, a rigorous structural proof is absolutely necessary. We turned therefore to X-ray crystallographic analysis which was performed on the trimethylphosphite complex (**24c**), which turned out to yield more suitable crystals. The crystallographic work, the details of which will be published elsewhere,† has confirmed structure **24c** and therefore also **24b** and **24a**. A three dimensional computer drawing of **24c** is depicted in Fig. 2. Several important structural parameters are listed in Table 2. The bonding distances between the Fe atom and the three π carbon, C(22), C(23) and C(24) are

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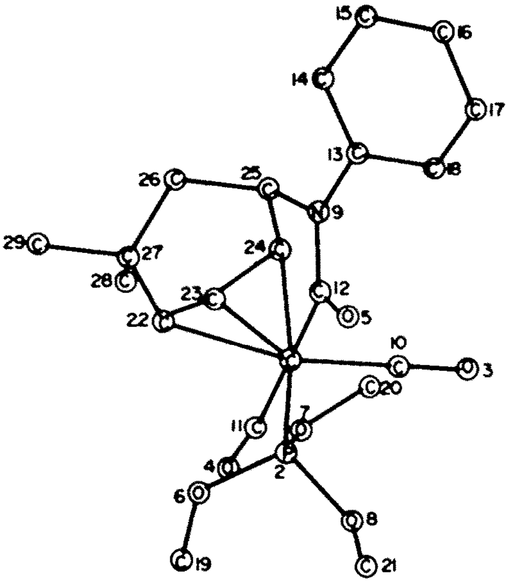


Fig. 2. Crystallographic structure of **24c**.

similar and in agreement with X-ray values in other $\pi$-allyl complexes.[8] The two bond distances among the three $\pi$ carbons, C(22)–C(23) and C(23)–C(24), are very similar and fall between the values of single and double bonds, implying a $\pi$-allyl delocalized structure. The two "$sp^2$–$sp^3$" hybridized bond distance, C(24)–C(25) and C(22)–C(24) are in agreement with the value of 1.51 Å, calculated by Sutton.[9] The distance of 2.02 Å for the Fe–C(12) bond, which is considerably longer than the two other Fe–CO bond distances (*ca.* 1.76 Å) implies a simple $\sigma$-bonding between the Fe atom and the carbamoyl moiety. A dihedral angle of 14.6° is subtended by the bond system C(23)–C(24)–C(25)–C(26) (Fig. 2). This is the consequence of a twist-boat geometry adopted by the carbocycle. A short non-bonding distance (3.189 Å) between C-(28) and C-(12) atoms is observed.

At this point a summary of the results is in place.

(a) All three oxazines **8**, **15** and **16** were treated with $Fe_2(CO)_9$ in benzene under comparable conditions.

(b) Oxazines **8**, **15** and **16** give rise to the Fe-free 4-membered ring lactams **11**, **21** and **25** respectively, in yields of *ca.* 10%. An isomeric lactam (**26**) was isolated in the case of oxazine **16** (eqn 7), as well as a cyclic carbamate (**23**).

(c) The two oxazines **8** and **15** give rise also to anilinocyclohexadiene complexes **12**(25%) and **22**(42%) respectively.

(d) A $\sigma$–$\pi$-allyl complex (**24a**) was isolated only in the case of oxazine (**16**).

(e) Neither in the reaction of **8** nor in that of **15** with $Fe_2(CO)_9$, could a complex analogous to **24a** be detected.

It now remains to elucidate the role of the complex **24a** in reaction (7). Its thermal decomposition in benzene led to a clean generation of two Fe-free products namely, **25** and **26**. The structures of these two compounds were assigned on the basis of their NMR and IR spectra (Table 1) and mass spectral and elemental analysis data (Experimental). Comparison of the IR and tlc of these two compounds with those of the original products' mixture from reaction (7), establishes beyond doubt that **25** and **26** are also formed in reaction (7). Most important is the fact that neither under the original reaction conditions (eqn 7) nor in the separate thermal decomposition of **24a**, an anilino cyclohexadiene complex analogous to **12** and **22** is formed.

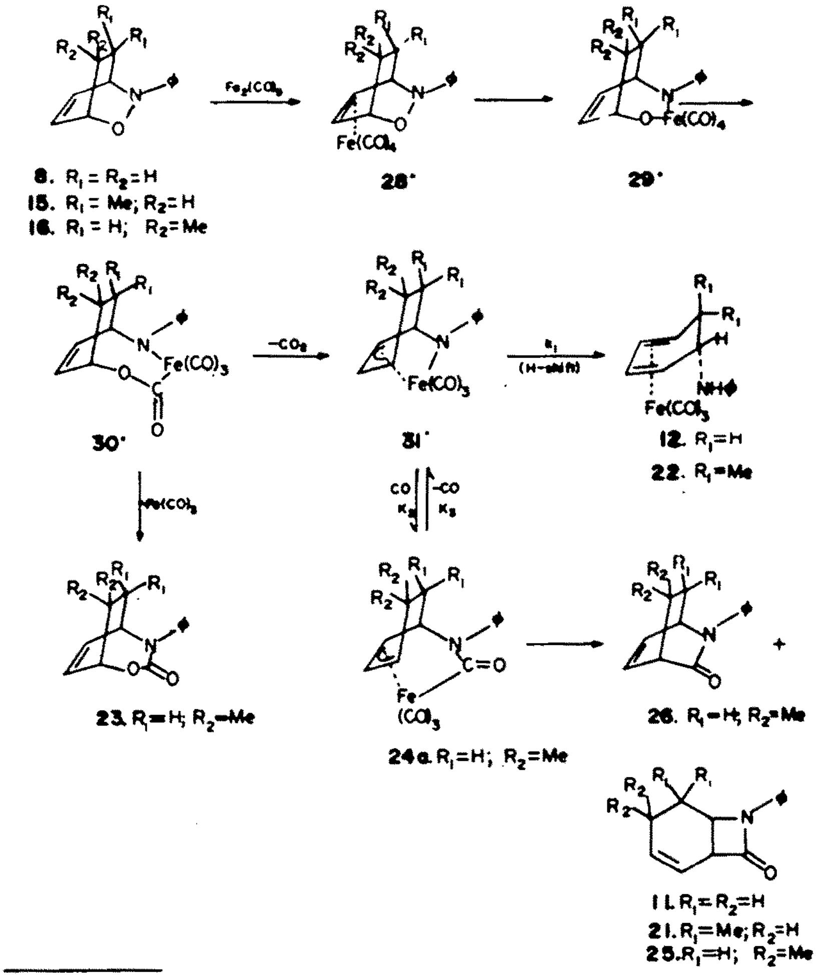
On the basis of the results presented hitherto, we suggest Scheme 1 as a plausible general reaction pathway which can account for most of the experimental facts. Part of this scheme is of course speculative.

From the results of the thermal reaction of **24a** we conclude that this is the immediate precursor of **25** and **26**. Furthermore, we are justified in claiming that this is a general reaction, i.e. lactams **11** and **21** are also formed from complexes analogous to **24a** (Scheme 1), although they could not be detected. Before proceeding further with our arguments, it is instructive to examine again the X-ray structure of **24a** which sheds light on the mechanism of these reactions. Figure 2 reveals a highly congested array of atoms in the vicinity of the carbamoyl group. Table 1 indicates extraordinary short non-bonding distance between C-(24) and C-(12) (2.727 Å) and also between C-(22) and C-(12) (3.183 Å). In fact, these two non-bonding interactions in the intermediate **24a** become bonding interactions in the lactams **25** and **26**. Thus the CO of the carbamoyl group and the two terminal C atoms of the $\pi$ allyl system of **24a** are brought into reacting distance in the coordination sphere of the iron, leading to ring closures at the above two terminii. The reversibility of the reaction, i.e. **25**→**24** with $Fe_2(CO)_9$ was examined by subjecting the lactam **21** to the original reaction condition. But, **21** was totally inert under these reaction conditions, and was recovered unchanged.

Two important points remained to be clarified. The first one concerns the mode of formation of **24a** and the

Table 2. Selected bond distances in **24c** (see Fig. 2)

| Bond | r(Å) | Bond | r(Å) |
|---|---|---|---|
| Fe-C(22) | 2.171(6) | C(22)-C(27) | 1.541(13) |
| Fe-C(23) | 2.042(7) | Fe -C(12) | 2.022(10) |
| Fe-C(24) | 2.115(8) | Fe -C(10) | 1.773(7) |
| C(22)-C(23) | 1.419(11) | Fe -C(11) | 1.786(8) |
| C(23)-C(24) | 1.410(12) | C(28)-C(24) | 4.078(8) |
| C(24)-C(25) | 1.542(13) | C(28)-C(12) | 3.189(10) |
| | | C(24)-C(12) | 2.727(11) |
| | | C(22)-C(12) | 3.183(8) |



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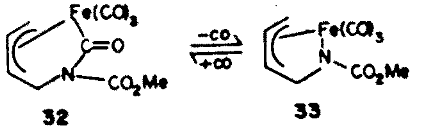
*The structures marked with * represent intermediates which were not isolated.

Scheme 1.

analagous (assumed) complexes originating from 8 and 15. The second question concerns the identity of the immediate precursor of the anilino cyclohexadiene complexes 12 and 22. Blocking the formation of the cyclohexadiene complex in 16 with the concomitant isolation of the labile intermediate 24a (eqn 7) does not necessarily prove that the latter is the immediate precursor of the former in those systems where such dienes complexes are formed (eqns 3 and 6). This implies the existence of additional intermediate(s) in the reaction pathway. Indeed, since the thermal decomposition of 24a does not generate the cyclic carbamate 23, at least one such intermediate may precede the formation of 24a (Scheme 1). The most logical one has been assigned structure 30 (Scheme 1), which is transformed to 23 by losing the element of Fe(CO)₃. Central to the formation of 30 and Scheme 1 as a whole, is the oxidative addition to the >N–O– bond (via an initial monoene complex such as 28). Such a step is compatible with the known energy of the >N–O– bond (53 kcal/mol). Granted that 29 is the primary reaction intermediate, its transformation to 30 represents insertion of CO to the O–Fe-bond, a process acceptable in organometallic chemistry (*vide infra*). This second intermediate, 30, may account for two experimental facts: (a) the formation of 23, as was previously stated (b) the loss of $CO_2$ which was recorded experimentally in the reaction of 8 with $Fe_2(CO)_9$. Important to structure 31 and to the rest of the scheme is the recent finding of the reversible reaction



system (32 ⇌ 33) by Aumann.[4] The starting material for this system is the N-carbomethoxy vinylaziridine and $Fe(CO)_5$. Both 32 and 33, which are structurally analogous to 24a and 31 respectively, are relatively stable and isolable compounds. We suggest that 31 is a common intermediate in two competing reactions. The first one is the formation of the dienes 12 and 22, which occurs by shift of H atom (31; $R_2 = H$) from carbon to nitrogen allowing the development of the 1,3-diene system.[4] The *endo* configuration of the product (12, 22) is compatible with the geometry of 31. Clearly, when $R_2 = Me$ this reaction is being blocked ($K_1 = 0$). Consequently the reaction is being diverted to 24a by CO insertion, and 24a then decomposes thermally to the Fe-free lactams as previously discussed. Thus, when 8 and 15 react with $Fe_2(CO)_9$ ($R_2 = H$), the product distribution, 12/11 and

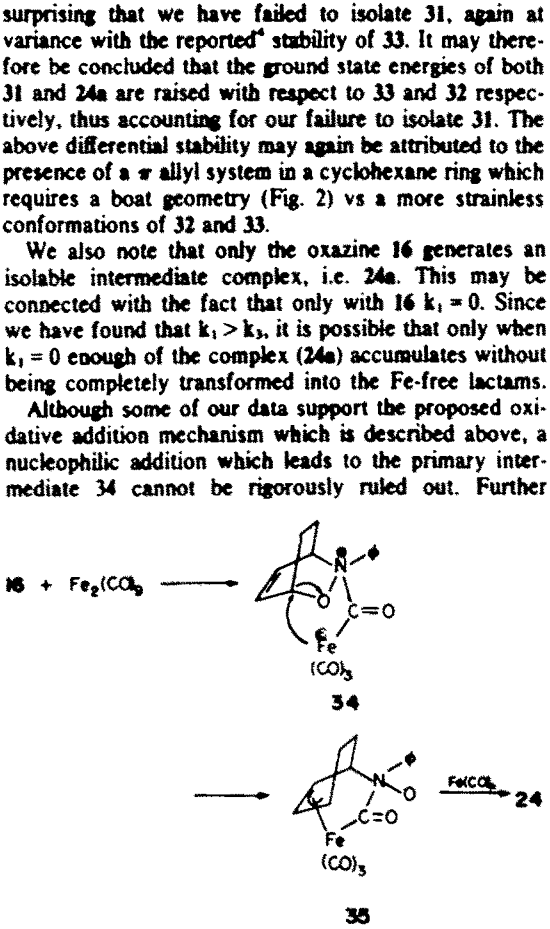
22/21 depends on the ratio $k_1/k_2$, provided $k_3 = 0$. The experimental ratio is *ca.* 3. Although not required for the sake of argumentation, we have entered the reversible decarbonylation reaction ($k_3$) into Scheme 1, since from Aumman's report[4] it is apparent that $k_3 > k_2$, although the two reactions were performed under different conditions.

A disturbing point in the reaction pathway represented in Scheme 1, is our failure to isolate **31** ($R_2$ = Me) which is analogous to the stable **33**, isolated by Aumman.[4]

We recall that **24a** is an extremely unstable compound, at variance with the reported[4] stability of **32** and also of **4**.[10] Since from structural consideration **31** must be thermodynamically even less stable than **24a**, it is not surprising that we have failed to isolate **31**, again at variance with the reported[4] stability of **33**. It may therefore be concluded that the ground state energies of both **31** and **24a** are raised with respect to **33** and **32** respectively, thus accounting for our failure to isolate **31**. The above differential stability may again be attributed to the presence of a π allyl system in a cyclohexane ring which requires a boat geometry (Fig. 2) vs a more strainless conformations of **32** and **33**.

We also note that only the oxazine **16** generates an isolable intermediate complex, i.e. **24a**. This may be connected with the fact that only with **16** $k_1 = 0$. Since we have found that $k_1 > k_3$, it is possible that only when $k_1 = 0$ enough of the complex (**24a**) accumulates without being completely transformed into the Fe-free lactams.

Although some of our data support the proposed oxidative addition mechanism which is described above, a nucleophilic addition which leads to the primary intermediate **34** cannot be rigorously ruled out. Further nucleophilic displacement by iron may lead to the amine oxide **35**, which should be readily reduced by iron carbonyl present in solution.[11]



## EXPERIMENTAL

*General.* M.ps were determined with Thomas and Hoover apparatus and are uncorrected. IR 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 using the following instruments: Atlas CH4, Perkin Elmer Hitachi RMU-6 and Du Pont 21-491B, using direct inlet system and ionization potential of 60 eV. All reactions involving Fe complexes were carried out under $N_2$ which was purified on W/Cu column at 300°, dried over $H_2SO_4$ and then passed over KOH and glass wool columns.

***Reaction of* 8 *with* $Fe_2(CO)_9$.** A soln of **8**[10] (2 g; 10.7 mmoles) in benzene (40 ml) and $Fe_2(CO)_9$ (4 g; 11 mmoles) was stirred at 40° for 20 min. The mixture was filtered and the oily residue left after evaporation of the solvent was chromatographed on basic alumina. Pet.-ether eluted a yellow crystalline substance **12** which was cryst. from hexane (25%). For physical data see Ref. 1*a*. (Found: C, 57.96; H, 4.26; N, 5.09. Calc. for $C_{15}H_{13}FeNO_3$: C, 57.90; H, 4.18; N, 4.51%).

The mother liquor from the above crystallization was purified by preparative tlc (silica) using benzene–pet. ether 1:2 yielding **10**, (6%) as an oil, NMR ($CDCl_3$, δ): 7.14 (m, 2H), 6.65 (m, 3H), 5.68 (m, 2H), 3.62 (m, 1H), 3.38 (m, NH), 2.10 (m, 6H). IR (neat): 3360 (NH) $cm^{-1}$. *m/e* 173 ($M^+$, $C_{12}H_{15}N$). Benzoylation of **10** yielded a solid, m.p. 89–89.5°, lit.[10] 72.5–74.5°, *m/e* 277 ($M^+$, $C_{19}H_{19}NO$).

Further elution with 15% $CH_2Cl_2$–pet. ether yielded **11**, solid 8%, which was sublimed (60°/0.01 mm), m.p. 76.5–77°, *m/e* 199($M^+$), 80($M^+$-ϕNCO). For other physical data, see Ref. 1*a*. (Found: C, 78.42; H, 6.40; N, 7.11. Calc. for $C_{13}H_{13}NO$: C, 78.40; H, 6.54; N, 7.04%).

Methylene chloride eluted **9**(8%), solid, sublimed (58°/0.01 mm), cryst. from hexane, m.p. 64.5–65.5°, lit.[10] 64.5–65.5°.

exo-5-*Anilino*-1,3-*cyclohexadiene irontricarbonyl* was prepared by quenching cyclohexadienylium irontricarbonyl tetrafluoroborate in $CH_2Cl_2$ with aniline, solid, cryst. from hexane, yellow needles, m.p. 84.5°, NMR (see Fig. 1a in Ref. 1*a*).

*8,8- and 9,9 - Dimethyl - 3 - phenyl - 2 - oxa - 3 - azabicyclo[2.2.2]oct - 5 - ene* (**15**) *and* (**16**). A soln of nitrosobenzene (3.9 g) and 5,5 - dimethyl - 1,3 - cyclohexadiene (5 g) in ether (50 ml) was kept at 3° for 15 hr. The solvent was evaporated and the residual oil was chromatographed on a dry column of silica using benzene. First there was obtained a solid, **15**, 5.57 g (72%), cryst. from pet.-ether, sublimed (30°/0.005 mm), m.p. 52–3°, NMR presented in Fig. 1(b). (Found: C, 78.04; H, 8.15; N, 6.62. Calc. for $C_{14}H_{17}NO$: C, 78.1; H, 7.9; N, 6.51%). The above was followed by **16**, 2.24 g (28%), cryst. from pet.-ether, sublimed (30°, 0.005 mm), m.p. 66–67°. NMR data presented in Fig. 1(a). (Found: C, 77.74; H, 7.68. Calc. as for **15**).

cis - *Cyclohex - 4 - anilino - 5,5 - dimethyl - 2 - ene - 1 - ol* (**17**). Compound **15** (200 mg) in HAc (5 ml) was treated with Zn (0.5 g). After 15 hr at room temp. the mixture was filtered, basified with NaOH, washed with ether which was dried ($K_2CO_3$) and evaporated. The residue (150 mg) was cryst. ether–pet. ether (1:5), m.p. 78–78.5°. NMR ($CDCl_3$, δ): 7.15 (m, 2H), 6.65 (m, 3H), 5.74 (s, 2H), 4.21 (t, J = 7 Hz, 1H), 3.51 (m, 1H), 2.6 (broad, NH, OH), 1.63 (dq, J = 14, 7 and 6 Hz, 2H), 1.00 (s, 6H).

Acetylation of **17** (500 mg) was performed in pyridine–$Ac_2O$ soln (1:1) at room temp. for 15 hr. The soln was diluted with ice water, and the product was extracted with $CH_2Cl_2$ which was washed with dil. HCl followed by $NaHCO_3$ and sat. NaCl aq. Evaporation of the solvent left an oil, **19**, 600 mg, homogenous by tlc. NMR (δ, $CDCl_3$): 7.15 (m, 2H), 6.66 (m, 3H), 5.75 (m, 2H), 5.28 (m, 1H), 3.6 (m, 1H), 3.3 (m, 1H), 2.25 (d, J = 3 Hz, 1H), 2.05 (s, 3H), 1.73 (d, J = 6 Hz, 1H), 1.04 (s, 3H), 1.03 (s, 3H). IR($CHCl_3$): 3420 (NH), 1730 (C=O) $cm^{-1}$, *m/e* ($M^+$, $C_{16}H_{15}NO_2$).

cis - *Cyclohex - 4 - anilino - 6,6 - dimethyl - 2 - ene - 1 - ol* (**18**). Compound **16** was reduced (Zn/HAc) as described for **15**. The crude was dissolved in benzene, and washed with 5% HCl aq., which was basified (NaOH) and washed with $CH_2Cl_2$. Evaporation of the solvent yielded **18**, 0.1 g, sublimed (160°/0.01 mm), m.p. 107–8°. NMR ($CDCl_3$, δ): 7.15 (m, 2H), 6.65 (m, 3H), 5.8 (m, 2H), 3.92 (dd, J = 8.2 and 6.8 Hz, 1H), 3.52 (m, 1H), 2.85 (br., s, 2H), 1.55 (m, 2H), 0.95 (s, 3H), 0.91 (s, 3H). IR($CHCl_3$): 3570 (OH free), 3390 (OH bonded) $cm^{-1}$, *m/e* 217 ($M^+$, $C_{14}H_{14}NO$).

The benzene phase was dried and evaporated. The residue, **20**, 0.07 g was sublimed (90°/0.01 mm), m.p. 117–18°. NMR ($CDCl_3$, δ): 7.25 (m, 5H), 5.8 (m, 2H), 5.08 (dd, J = 9.8 and 7.5 Hz, 1H), 3.35 (br. d, J = 4 Hz, 1H), 2.08 (m, OH), 1.78 (s, 3H), 1.5 (m, 2H), 0.9 (s, 6H). IR($CHCl_3$): 3570 (OH free), 3400 (OH bonded), 1650 (C=O) $cm^{-1}$, *m/e* 259 ($M^+$, $C_{16}H_{15}NO_2$).

***Reaction of* 15 *with* $Fe_2(CO)_9$.** The reaction and isolation of products were carried out as described for **8**. endo - 5 - *anilino - 6,6 - dimethyl - cyclohexa - 1,3 - diene irontricarbonyl* (**22**), was obtained (42%, yellow needles, m.p. 60–61° (hexane). NMR and IR data are presented in Table 1; *m/e* 341 ($M^+$), 213 ($M^+$-CO), 185

($M^+$-2CO), 157 ($M^+$-3CO). (Found: C, 60.65; H, 5.14; N, 4.81. Calc. for $C_{17}H_{17}FeNO_3$: C, 60.25; H, 5.01; N, 4.14%).

cis - 5,5 - *Dimethyl - 7 - phenyl - 7 - azabicyclo[0.2.4]oct - 2 - ene - 8 - one* (21) was isolated (9%), sublimed (65°/0.01 mm), needles from hexane, m.p. 119–120°. NMR and IR data are presented in Table 1; *m/e* 227 ($M^+$, $C_{15}H_{17}NO$), 108 ($M^+$-$\phi$NCO).

The amino alcohol 17 was isolated (28%) and was found to be identical with the reduction product of 15 (Zn/HAc).

*Reaction of* 16 *with* $Fe_2CO_9$. A suspension of $Fe_2(CO)_9$ (3.25 g; 9 mmoles) in a soln of 15 (1.0 g; 4.65 mmoles) in benzene–pet. ether 1:1 (20 ml), was stirred under $N_2$ at 33° for 3 hr. The dark soln was filtered under $N_2$ and the solvent was evaporated. The residue was chromatographed under $N_2$ on a column of basic alumina cooled with ice water. The column was washed with pet. ether, and $CH_2Cl_2$ eluted on oil, 24a, 0.515 g (30%), homogenous by tlc, which was stable when kept at 0° under $N_2$. NMR and IR data are presented in Table 1.

$CH_2Cl_2$ eluted a second solid, 23, cryst. from ether–pet.-ether, (6%), m.p. 152–152.5°. NMR ($CDCl_3$, $\delta$): 7.28 (m, 5H), 6.64 (m, 2H), 4.26 (dd, J = 5 and 2 HZ, 1H), 3.71 (m, 1H), 2.27 (dd = 14 and 3 Hz, 1H), 1.59 (dd, J = 14 and 5 Hz, 1H), 1.41 (s, 3H), 0.97 (s, 3H). IR($CDCl_3$): 1680 (C=O) $cm^{-1}$. (Found: C, 73.01; H, 7.17; N, 5.96. Calc. for $C_{15}H_{17}NO_2$: C, 72.8; H, 7.17; N, 5.67%). *m/e* ($M^+$ 243).

4 - *Aniline - 6,6 - dimethyl - π - cyclohexallyl - carboxyiron - dicarbonyl triphenylphosphine lactam* (24b). A mixture of 24a (0.108 g; 0.295 mmoles) triphenylphosphine (0.078 g; 0.297 mmoles) and benzene (3 ml) was stirred under $N_2$ at room temp. for 2 hr. The solvent was removed *in vacuo*, the residue triturated with pet. ether and cryst. (3x) from pet. ether, yellow needles 24b, 0.101 g, m.p. 139–140°. NMR and IR data are presented in Table 1. (Found: C, 68.7; H, 5.42; N, 2.40; Fe, 8.83. Calc. for $C_{35}H_{32}FePNO_3$: C, 69.9; H, 5.33; N, 2.33; Fe, 9.28%).

4 - *Anilino - 6,6 - dimethyl - π - cyclohexallyl - carboxy - irondicarbonyl trimethylphosphite lactam* (24c). The adduct 16 was reacted with $Fe_2(CO)_9$ as previously described. After filtration of the dark soln, trimethylphosphite (0.472 g) in benzene (6 ml) was added and the soln was stirred under $N_2$ at room temp. for 2 hr. After evaporation of the solvent, the residue was chromatographed on basic alumina. $CH_2Cl_2$ eluted 24c, 1 g, homogenous by tlc. Cryst. (3×) from hexane under $N_2$ gave yellow prisms, m.p. 129–130° (dec). NMR ($C_6D_6$, $\delta$): 7.2 (m, 5H), 5.27 (m, 1H), 5.07 (m, 1H), 4.19 (m, 1H), 3.92 (m, 1H), 3.31 (d, $J_{P\text{-}OMe}$ = 11 Hz, 9H), 1.66 (s, 3H), 1.24 (s, 3H), 1.1 (dq, J = 13 and 4 Hz, 2H). IR($CHCl_3$): 1555 (NCOFe) $cm^{-1}$; (hexane): 2020, 1960 (C≡O) $cm^{-1}$. (Found: C, 49.56; H, 5.10; N, 3.01; P, 6.17; Fe, 11.12. Calc. for $C_{20}H_{26}FePNO_6$: C, 51.80; H, 5.62; N, 3.02; P, 6.68; Fe, 12.05%). A single crystal X-ray analysis was performed on this substance.

*Thermal reaction of* 24a. The lactam 24a (500 mg) in benzene (15 ml) was refluxed (80°) for 5 min. The solvent was evaporated and the residue chromatographed on basic alumina.

$CH_2Cl_2$–pet.-ether (1:1) eluted a crystalline substance (25), sublimed (100°/0.05 mm), m.p. 85–85.5°. Spectral data are presented in Table 1: *m/e* 227 ($M^+$), 108 ($M^+$-$\phi$NCO). (Found: C, 79.41; H, 7.52; N, 6.34. Calc. for $C_{15}H_{17}NO$: C, 79.40; H, 7.48; N, 6.17%).

Further development of the column with $CH_2Cl_2$ eluted 2, 5%, m.p. 111–112° (hexane). Spectral data are presented in Table 1; *m/e* 227 ($M^+$).

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