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REACTION OF TRANSITION METAL CARBONYLS WITH HETEROCYCLIC SYSTEMS—II

DIIRONNONARCARBONYL AND 1,2-OXAZINES

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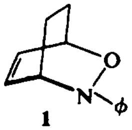
Abstract—The reactivity of the >N—O— bond towards diironnonacarbonyl was investigated. 3,6-Dihydro and tetrahydro-1,2-oxazines were used as model compounds. Reduction of the >N—O— bond predominates in presence of water, while under anydrous conditions a CO insertion into the >N—O— bond of tetrahydro-1,2-oxazine takes place. The 3,6-dihydro-1,2-oxazine in the presence of $Fe_2(CO)_9$ and water, yield π-allyl-Fe-σ-lactones. Carbon dioxide and aniline are also formed in this reaction. The amino alcohol 7 is an intermediate in this and analogous reactions. The lactone 3 under Al_2O_3 catalysis reacts with primary amines to yield the corresponding lactams. Mechanistic investigation of this reaction points towards a S_N2'-like mechanism inasmuch as the attack of the base occurs on the terminal carbon of the π-allyl system. The lactam 4 could be readily converted into the complex π-crotonylideneaniline iron tricarbonyl for which an intramolecular 1,4-H shift was demonstrated by a labeling experiment with deuterium.

INTRODUCTION

The interaction of zero valent complexes of transition metals with heterocyclic compounds gives rise to systems with interesting chemical reactivity. Both olefins and heteroatoms are known for their reactivity towards transition metal complexes. By incorporating these elements of reactivity into a single molecular structure, unique reaction courses were anticipated and indeed were realized. Furthermore, close distance interactions in such systems and the unique complexing capacity of the metal atom may lead to intramolecular trapping of transient species, thus raising the probability of isolating intermediates which are otherwise difficult to obtain. Thus, the carbonyl metal complex is expected to bring about a chemical change and then possibily trap the unstable reaction product which may be formed. Such an approach provides an additional mechanistic tool for the study of transition metal chemistry. Indeed, this approach was found promising, and the results of the reaction of N-phenyl-2-oxa-3-azabicyclo [2.2.2]oct-5-ene with ironnonacarbonyl[1] prompted us to investigate the scope and mechanisms of these reactions.

RESULTS AND DISCUSSION

The bicylic oxazine 1 was found to react rapidly with $Fe_2(CO)_9$ in benzene at *ca* 40°. Four products were isolated and their structures were assigned.[1] The common reaction feature which characterizes all the four products is the cleavage of the N—O bond, which indeed is the weakest bond in 1. In the present study we have extended the investigation to the monocyclic analog of 1, N-phenyl-3,6-dihydro-1,2-oxazine 2, and compounds of related molecular structures. Although the two compounds contain identical functional groups, their reactions with diironnonacarbonyl followed completely different paths. In variance with the four products isolated from the reaction of 1 and $Fe_2(CO)_9$, a single compound, or two compounds, depending on the work-up of the reaction mixture, was obtained when 2



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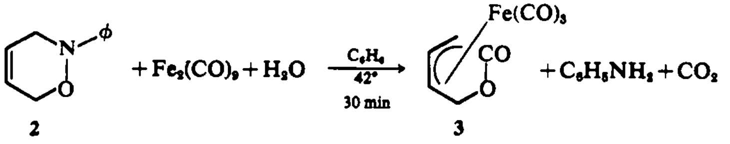
was allowed to react with $Fe_2(CO)_9$ (Eq 1). The most important feature of this reaction is the presence of at least equimolar quantity of water, which was deliberately added to the dried benzene solvent. Otherwise, apparently, the reaction took a different course which could not be elucidated. Aniline was qualitatively determined in the product mixture, and an equimolar quantity with respect to the oxazine **2** of CO_2 was evolved. The m.p. and all spectral properties of **3** were found to be identical with those of a compound which was synthesized by us according to a published procedure.[2] The π-allyl-Fe-σ-lactone structure **3** was assigned to a compound which was obtained by two different investigators who employed different synthetic routes.[2,3] These reactions will be discussed later, however, all the analytical and spectral data support the above molecular structure **3**.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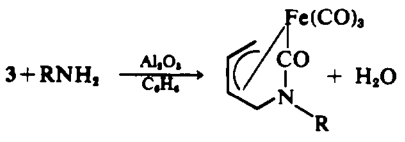
(2)

4a: R = Ph
b: R = Me
c: R = H

When the lactone **3** in benzene was stirred for 2 h at room temperature with primary amines and in the presence of basic or neutral alumina the corresponding lactams (Eq 2) were obtained in high yields. Thus, **4a** and **4b** were obtained by treating **3** with aniline and methylamine respectively. The above reaction did not occur when alumina was omitted. In fact, the aniline is a by-product in the lactone formation reaction (Eq 1) and is totally unreactive. If this product mixture, containing the aniline, is now passed through a column of alumina, the lactone is again quantitatively converted to the lactam **4a**. An attempt to obtain **4c** using ammonia, failed, probably due to the limited solubility of the latter in benzene. When ammonia in ether was used, the lactone **3** was unexpectedly converted into the π-butadiene iron tricarbonyl complex, also observed by Murdoch[3] although under different reaction conditions.

Lactams such as **4** have not been previously reported. A related acyclic system possessing similar structural features, $(CH_3)_2NCOFe(CO)_2C_5H_5$ was reported by King.[4] The subject of carbomoyl complexes of transition metals was recently reviewed by Angelici.[5]

The structure of **4a** was assigned on the basis of elemental analysis, ($C_{14}H_{11}FeNO_4$), and mass spectrum (*m/e* 313, followed by four intense lines which correspond to stepwise loss of CO groups). The intense IR band at 1580 cm^{-1} was assigned to the stretching vibration of the CO in the NCOFe structure.* The lactone **3** exhibits the corresponding CO band at higher frequency (1665 cm^{-1}). A convincing proof for the structure of **4a** and also of **3** was adduced from analysis of the NMR spectra. The aliphatic protons of **4a** comprise a 6-proton extensively coupled system, resonating within a range of 2 ppm (Fig 1). Unequivocal assignments of these lines were required for further mechanistic studies, as well as for structural proof. Therefore, in order to simplify the spectrum, the two d_2 and d_4-lactams **5** and **6**, as well as the corresponding lactones **5a** and **6a** were prepared according to Eqs 3 and 4.

The mixtures from the reactions of the two deuterio oxazines with $Fe_2(CO)_9$ were not purified, but directly converted to the corresponding lactams **5** and **6** via chromatography on alumina. The corresponding lactones **5a** and **6a** were crystallized from the reaction mixture without contact with alumina. The NMR spectra of **5** and **6** are presented in Figs 2 and 3 respectively. The spectrum of **5** (Fig 3) consists of an AB quartet and two singlets which must be assigned to two pairs of protons at C-1 and C-4. In principle, since the molecule is chiral, each pair should exhibit an AB quartet. The two singlets must be assigned to the terminal C-1

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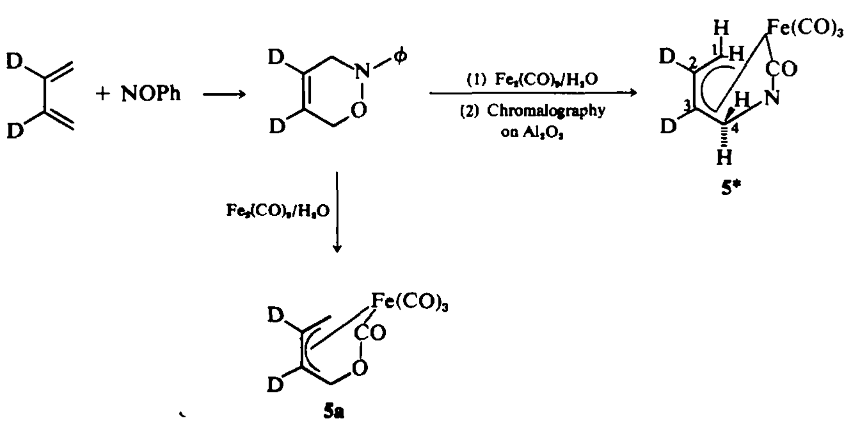
*IR spectra of N,N-dimethylcarbomoyl ligands[5] show characteristic C=O stretching absorption in the range 1565–1615 cm^{-1}.



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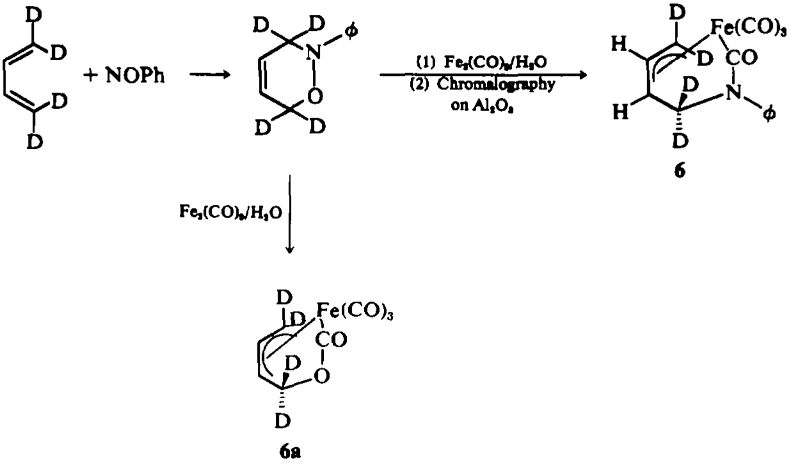

(4)

protons, since very small spin couplings were previously recorded for terminal protons of π-allyl systems.[2] The assignment of the AB quartet. (J = 12 c/s) to the C-4 protons is in accord with the known large spin coupling of geminal protons at a saturated carbon.[6] As anticipated, the spectrum of 6 (Fig 2) exhibits only an AB quartet which must be assigned to the two protons at C-2 and C-3. With the aid of the spectra of the two deuteriolactams, all the signals in the H-spectrum of 4a (Fig 1) can now be identified and assigned to the proper H atoms, and all spin couplings can be determined. The pattern of the NMR spectrum of 4b is very similar to that of 4a but for the N-Me signal at 2·56 ppm. This analysis leaves no doubt as to the molecular structure assigned to the lactams 4a and 4b. Taking into account variations in the chemical shifts, the patterns of the NMR spectra of the lactones 5a and 6a were very similar to those of the corresponding lactams, and the assignments were made according to the above line of reasoning. Thus, aside from unequivocal structural proof, we could also now assign all the lines (and spin couplings) to the proper protons in the H-spectrum of the lactone 3 which will become important in the subsequent discussion.

Once the molecular structures of 3 and 4 were established, we focused our attention on the nature of the reactions involved in their formation. Turning to the primary reaction of the oxazine with $Fe_2(CO)_9$ which results in the formation of the π-allyl-Fe-σ-lactone (Eq 1), it is remarkable that aniline is being split off. In view of the fact that the reaction requires at least equimolar quantity of water, we have suspected that the initial step involves reduction of the N—O bond. Indeed, quenching of the reaction after *ca* 10 min reveals the presence of *cis*-4-anilino-2-buten-1-ol 7. When, in a separate experiment, this intermediate was subjected to the action of $Fe_2(CO)_9$ under *anhydrous*

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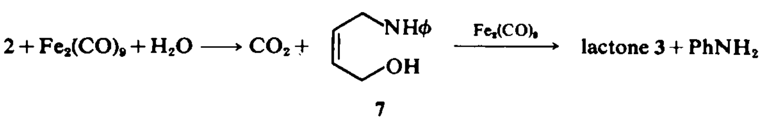
*Numbering of the carbons is arbitrary and does not correspond with the nomeclature used in this text.



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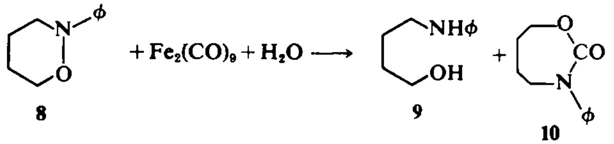
(5)

conditions (Eq 5), aniline and the lactone **3** were isolated. By repeating the reaction of the oxazine with $Fe_2(CO)_9$ under anhydrous conditions, neither **7** nor **3** could be detected. In conclusion we have established that the reaction under investigation is a two step sequence with the anilino-alcohol as an intermediate. Furthermore, it was ascertained that it is the first step that requires one mole of water and is also responsible for the formation of CO_2, while each step requires one mole of the diironnonacarbonyl. This also accounts for the fact that low yields of the final lactone were encountered when less than two moles of $Fe_2(CO)_9$ per mole of the oxazine were used.

As far as the reductive step is concerned we have found that the double bond is not an essential structural feature. Thus, reaction of the tetrahydro oxazine derivative **8** with $Fe_2(CO)_9$ and water yielded the corresponding 4-anilino-butan-1-ol **9** which was now also accompanied by N-phenyl tetramethylene carbamate **10**, (Eq 6).* Neither of the products (Eq 6) could be converted into the other under the original reaction conditions. Thus neither of them serves as a precursor for the formation of the other. The rate of formation of the anilino alcohol **9** could be suppressed by the exclusion of water, and the carbamate **10** was practically the sole product of this reaction. Thus, the present reaction may turn out to be a satisfactory method for the reduction of a N—O- bond under neutral and very mild conditions (*ca* 1 h at 42° in benzene). Also, we are unaware of a previous case of insertion of a CO group into a N—O bond via metal carbonyls. The synthetic and mechanistic aspect of this reaction are being further pursued.



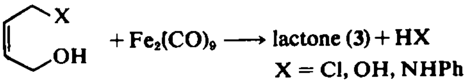
8 9 10

(6)

We have no experimental results to support a mechanistic rationale for the reductive step. Several related phenomena are recorded in the literature.

Iron carbonyls are known to form hydrido complexes in strong base.[7] Recently the reduction of conjugated double bonds with $Fe(CO)_5$ in sodium hydroxide was demonstrated.[8] The same authors have shown that such a reduction can also be achieved with ironpentacarbonyl, tertiary amine base and water. Clearly such a mixture must possess reductive capacity. Aromatic nitro compounds were also reduced with iron carbonyl complexes to the corresponding anilines.[9] Edgell *et al*[10] have investigated the interaction between iron carbonyl and secondary nitrogen bases.

The second step of the reaction (Eq 5), also affected by the ironcarbonyl, is accompanied by extensive structural alterations. The product lactone **3**, was previously obtained in very similar reactions, using *cis*-4-chloro-2-buten-1-ol[2] or *cis*-2-buten -1,4-diol[3] and iron carbonyls. In fact, **3** was prepared by us using the former starting material. It seems that the reaction is general and can be formulated by Eq 8. The reported yields of **3** when X is Cl and OH are 25 and 80% respectively. In our case (X = NHϕ) **3** was formed in 78%. Inasmuch as this reaction does occur with the three quite different X groups and under very mild conditions, it seems that it is indiscriminate in X. However, we have succeeded in modifying its course by increasing the basicity of the nitrogen atom. Thus when *cis*-4-methylamino-2-buten-1-ol **11** was reacted with $Fe_2(CO)_9$ the N-methyl lactam **4b**, identical with the lactam of Eq 2, rather than lactone **3**, was obtained (Eq 9). It could be argued that the lactone **3** was formed also in this case and then further reacts with the liberated methylamine, to give the lactam **4b**, as generally described in Eq 2. However, this possibility is excluded since methylamine fails to react with the lactone **3** without Al_2O_3 catalysis.



(8)

The insolubility of *cis*-4-amino-2-buten-1-ol in

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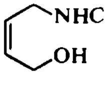
*It is interesting that the corresponding unsaturated carbamate could not be detected in the product mixture of Eq 5 when performed under wet or dry conditions. All spectral and analytical data are in accord with the structure assigned to **10**. (Experimental) benzene prevents its reaction with $Fe_2(CO)_9$, and the starting material was re-isolated. However, when 1,4-dihydro-1,2-oxazine **12** was reacted with $Fe_2(CO)_9$ in the presence of water the lactam **4c** was again obtained (Eq 10). It should be recalled that this lactam could not be obtained by reacting **3** with ammonia.



+ $Fe_2(CO)_9 \longrightarrow$ lactam **4b** (9)

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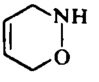
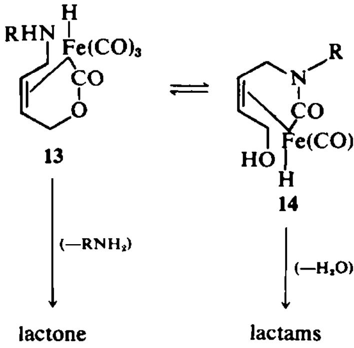


+ $2Fe_2(CO)_9 + H_2O \longrightarrow$ lactam **4c** (10)

12

In an attempt to explain the reaction of *cis*-2-buten -1,4-diol, and related alkyl derivatives, Murdoch[3] postulates an intermediate which in our case would correspond to **13**, and which would then eliminate RNH_2 (R = Ø) to yield the lactone **3**. Alternatively and analogously, intermediate **14** must be invoked to account for the formation of the lactams **4b** and **4c**, when R is Me and H, respectively. On grounds of relative basicity of N *vs* 0 and the relative stabilities of **13** and **14** it is not at all clear why **13** should be formed. However, if the above two intermediates are in equilibrium the difference in their stability, as far as amide and ester resonance are concerned, is expected to be levelled off due to the strong electron donation (Fe→C═O). The lactone-lactam distribution would therefore depend on the four rate constants of the above system.



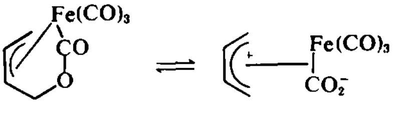
Turning to the reactions of the lactone **3** with amines (Eq 2), the formation of a lactam seems peculiar. Formally, Eq 2 represents an amidation reaction of a lactone. Interconversions of similar (but acyclic) carboalkyloxy and carbamoyl complexes were previously reported[5] (Eq 11) and are of course analogous to the corresponding reaction of ester-amide interchange. The conversion of **3** to **4** is unique inasmuch as it also involves the cleavage of the CH_2-O bond and preceeds under extremely mild conditions. Amidation of carbon lactones are known to require prolonged treatment at elevated temperatures. Three basic mechanistic interpretations can be invoked to account for this unusual conversion:

$$L\text{-}M\text{-}CO_2R + R'NH_2 \rightleftharpoons L\text{-}M\text{-}CONHR' + ROH \qquad (11)$$

(a) A direct substitution reaction by the amine on the saturated carbon atom of **3**, followed by dehydration of the resulting amino acid.

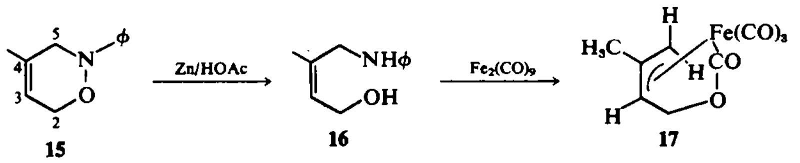
(b) Ionization of the CH_2—O bond followed by nucleophilic attack of the amine on the resulting carbonium ion. It must be noted that although the reaction conditions are not compatible with an ionization process, the resulting carbonium ion is anticipated to be stabilized by the adjacent π-allyl system (Eq 12).

(c) An S_N2'-type reaction, which involves an attack of the base on the terminal carbon (C-1) of the π-allyl system, a shift of the latter and departure of the carboalkyloxy group. This step must also be followed by dehydration of the resulting amino acid



(12)

The above three mechanistic possibilities can be distinguished by a labelling experiment (Eq 13). 4-Methyl-N-phenyl-3,6-dihydro-1,2-oxazine **15** was prepared by cycloaddition of nitrosobenzene to isoprene.[11] Apparently, only the 4-methyl isomer **15** is obtained.[11] Its structure was confirmed by NMR analysis (a singlet for the C-5 protons, which can be distinguished from the C-2 protons on the basis of its relative chemical shifts; the signal of the latter was split due to spin coupling with the C-3 proton). The anilino alcohol **16**, obtained by reduction of **15** with Zn/HOAc, was now reacted with $Fe_2(CO)_9$ and



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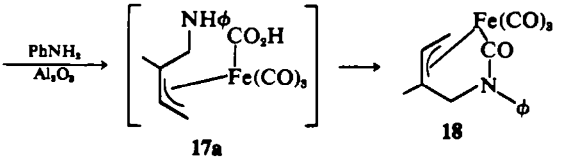


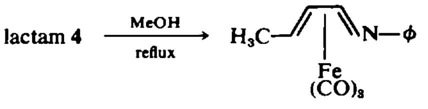
(14)

the Me group of this lactone retained its original position; on the basis of NMR analysis, structure 17 was assigned to this product. Thus, the signals of the terminal π-allyl protons, in the NMR spectrum of 17, which can now be readily identified from the spectrum of the di-deuterio derivative 5a, lack the *cis* and *trans* coupling with the adjacent proton clearly observable in the spectrum of the unsubstituted lactone (3), and appear as two singlets. The reaction of 17 with aniline and Al_2O_3 was now investigated. A single product was isolated from this reaction and structure 18 was assigned to it. The *cis* and *trans* coupling of the terminal π-allyl protons, discussed above, re-appeared in the NMR spectrum of the lactam 18, indicating a formal migration of the Me group. The conclusion that emerges from this experiment is that an S_N2'-type mechanism must be operative in the reaction of the lactone 17 with aniline leading to an intermediate amino-acid 17a which subsequently lactamizes to give the final product 18. Should a direct nucleophilic displacement on the saturated carbon have occurred, a non-rearranged product would exclusively be formed. A mixture of products would be anticipated from a delocalized carbonium ion intermediate (Eq 12). A strong doubt was recently cast on the very existence of a true S_N2' reaction mechanism.[12] Regardless of whether in the present case the reaction is concerted or develops intermediates, the exclusive formation of a rearranged product points towards the initial attack of the aniline at the terminal π-allyl system. The exact nature of the chemical events occurring after (or simultaneously with) the above step was not investigated here. It is worthy to note that unlike the common S_N2' -type nucleophilic displacements, four rather than three C atoms intervene between the entering nucleophile and the leaving group in the system under investigation.

It should be noted that the CO of the Fe-lactone is anticipated to be less reactive than a corresponding CO of a C-lactone toward addition of an amine. This must be due to the strong electron donation of $Fe \rightarrow C{=}O$ which is manifested by the unusually low infra red stretching frequency ($1665\ cm^{-1}$) of the carbonyl of 3. On the other hand the π-allyl system, due to electron donation to the iron, may consequently provide a better site for a nucleophilic attack.

If the introduction of the Me group in compound 8 does not perturb the reaction path, then we are justified in applying the same mechanistic rationalization to the reaction of the unsubstituted lactone 3 with aniline and most probably with any other nitrogen base.

In an attempt to probe into the chemistry of the



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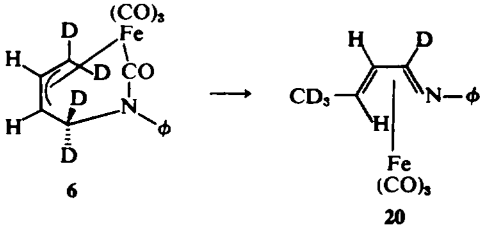

(15)

π-allyl lactam **4** it was found that short reflux in methanol transformed it (62%) into the crootonylideneaniline iron tricarbonyl complex **19**. Its structure was confirmed by synthesis. By using the tetra-deuterio lactam **6** we could ascertain the intramolecular nature of the reaction. Thus **20** was the sole product of this reaction (Eq 15). Its structure was deduced from the NMR spectrum which exhibits only an AX spectrum (J = 9·0 c/s) and no signal for Me protons. Thus, the reaction must involve an intramolecular 1,4-shift of H from C-4 to C-1.

EXPERIMENTAL

1-Hydroxymethyl-π-allylcarboxyiron tricarbonyl lactone **3**

Method A. A mixture of **2**[13] (1·61 g, 10 mmoles) and $Fe_2(CO)_9$ (7·28 g, 20 mmoles) in benzene (50 ml) containing H_2O (180 mg, 10 mmoles) was stirred under N_2 at 42–45°. Strong evolution of CO_2 started after 5 min and ceased after 20–30 min. The brown suspension was filtered through sinter glass under N_2 and evaporation of the filtrate yielded a brown semi-solid, 2·56 g. Careful crystallization from hexane gave **3** (40%), m.p. 112–114 dec (lit.[3] 115–116°, lit.[2] 118°). $\nu_{max}^{CHCl_3}$; 1665 cm^{-1} (OCOFe); ν_{max}^{hexane}; 2081, 2022 and 2002 cm^{-1} ($C\equiv O$). Mass spectrum *m/e* 238 (M^+), 210 (M^+—CO), 182 (M^+—2CO), 154 (M^+—3CO), 126 (M^+—4CO). Removal of aniline from the mixture by extraction with 5% HCl facilitated the purification of the product.

When the reaction vessel was connected to a trap of $Ba(OH)_2$ and swept with N_2, barium carbonate precipitated. In a separate experiment the CO_2 evolved was quantitatively determined by absorption on soda-lime, yield 107%, calcd on the basis of the water added.

Method B. A soln of *cis*-**7**[2] (1 g, 6 mmoles) and $Fe_2(CO)_9$ (3 g, 8·25 mmoles) in dry benzene (15 ml) was stirred under N_2 for 45 min. Filtration (fritte) and subsequent evaporation of the benzene left an oily residue which was dissolved in CH_2Cl_2 and washed with 5% HCl, water and dried over $MgSO_4$. Removal of the solvent gave a solid, which on crystallization from hexane-CH_2Cl_2 under N_2 at room temp gave **3**, 770 mg (78%), identical in all respects with the compound obtained by method A. Neutralization of the above acidic extracts with 10% NaOH, followed by extraction with CH_2Cl_2 gave aniline, 210 mg (56%).

1-Anilinomethyl-π-allylcarboxyliron tricarbonyl lactam **4a**

Method A. The previous reaction (method A) was repeated using the same amounts of reactants. After filtration, the benzene was removed at water pump pressure and the mixture was chromatographed on basic alumina (activity III). Washing of the column with hexane followed by hexane–CH_2Cl_2 (4:1) eluted a very labile material, 276 mg which decomposed immediately. Hexane–CH_2Cl_2 (1:1) eluted a yellow oil (**4a**), which solidified, 1·12 g (35%). Careful crystallization from CH_2Cl_2-hexane at room temp under N_2 gave prisms, m.p. 104–105°dec. (Found: C, 53·7; H, 4·71; N, 4·94; $C_{14}H_{11}FeNO_4$ requires: C, 53·6; H, 3·53; N, 4·47%), $\nu_{max}^{CHCl_3}$; 1580, (NCOFe), 1600, 1500 cm^{-1} (Ph); ν_{max}^{hexane}; 2080, 2020, 2000 cm^{-1} ($C\equiv O$). Mass spectrum *m/e* 313 (M^+), 285 (M^+—CO), 257 (M^+—2CO), 229 (M^+—3CO), and 201 (M^+—4CO). NMR (Fig 1).

Method B. Basic alumina (activity III, 4 g) was added to a soln of **3** (180 mg, 0·75 mmole) and 0·1 ml aniline in benzene (15 ml). After stirring at room temp for 2·5 h, the mixture was filtered, and the alumina was washed with CH_2Cl_2. Removal of the organic solvents and crystallization of the residue from hexane yielded 93 mg **4a** (40%). Using neutral alumina as a catalyst also yielded **4a** but at a slower rate (*ca* 4 h). No reaction occurs when silica was used as a catalyst or when no catalyst was employed.

1-Methylaminomethyl - π - allylcarboxyiron tricarbonyl lactam **4b**

Method A. To a soln of *cis* **11** (1 g, 9·9 mmoles) in dry benzene (45 ml), was added $Fe_2(CO_9)$(7·28 g, 20 mmoles) and the mixture was stirred for 50 min at 45°. The red soln was filtered, and evaporated at room temp under reduced pressure and the residue solidified. Purification with active carbon followed by crystallization from CH_2Cl_2-hexane yielded the N-Me lactam **4b**, 1·74 g (70%), m.p. 99–100° dec, $\nu_{max}^{CHCl_3}$; 1580 cm^{-1} (NCOFe); ν_{max}^{Hexane}; 2070, 2008 and 1998 cm^{-1} ($C\equiv O$). (Found: C, 43·24; H, 3·75; N, 5·49; $C_9H_9FeNO_4$ requires: C, 43·10; H, 3·59; N, 5·58%). Mass spectrum *m/e* 237 (M^+), NMR ($CDCl_3$, δ): 4·93 (m, 1H), 4·50 (m, 1H), 3·65 (dd, J = 8 and 1Hz, 1H), 3·38 (m, 2H), 2·85 (d, J = 12·5 Hz, 1H and 2·46 (s, 3H).

Method B. Compound **3** (300 mg, 1·25 mmoles) was dissolved in benzene (15 ml) saturated with methylamine and also containing basic alumina (3 g). After stirring for 3h at room temp, the mixture was filtered and the alumina washed with chloroform. Removal of the solvent left an oil which was chromatographed on basic alumina. With CH_2Cl_2, a substance was eluted, 140 mg (45%) identical in all respects with **4b** which was obtained by method A.

1-Aminomethyl - π - allylcarboxyiron tricarbonyl lactam **4c**

A mixture of 3,6- dihydro -1,2- oxazine[14] (1 g, 11·8 mmoles) in benzene (50 ml) containing H_2O (212 mg, 11·8 mmoles) and $Fe_2(CO)_9$ (8·56 g, 23·6 mmoles) was stirred under N_2 at 44° for 0·5 h. The red oil obtained after filtration and evaporation of the filtrate was chromatographed on basic alumina. The lactam **4c** was eluted with CH_2Cl_2, 43 mg, crystallized from ether-hexane. m.p. 106–107°, $\nu_{max}^{CHCl_3}$; 3465 (NH free), 3200 (NH bonded), 1595 cm^{-1} (NCOFe); ν_{max}^{hexane}; 2070, 2019 and 2000 cm^{-1} ($C\equiv O$). (Found: C, 41·14; H, 3·17; N, 5·76; $C_8H_7FeNO_4$ requires: C, 40·70; H, 2·95; N, 5·91%). Mass spectrum *m/e* 237 (M^+), NMR ($CDCl_3$, δ): 5·72 (m, $\underline{NH}$, 1H), 4·91 (m, 1H), 4·65 (m, 1H), 3·65 (d, J = 8 Hz, 1H), 3·38 (m, 2H) and 2·96 (d, J = 12 Hz, 1H).

4,5-d_2-N-Phenyl -3, 6- *dihydro* -1, 2- *oxazine and* 3, 3, 6, 6 - *d_4 - N - phenyl* - 3, 6 - *dihydro* - 1, 2 - *oxazine.* Both compounds were obtained by respectively reacting 2,3 - dideuterio - butadine[15] and 1,1,4,4 - tetradeuterio-butadiene[16] with nitrosobenzene under the usual conditions.[13] NMR of 4, 5-d_2 -N -phenyl -3, 6- dihydro- 1, 2-oxazine ($CDCl_3$, δ): 7·25 (m, 5H), 4·55 (t, J = 2 Hz, 2H), 3·82 (t, J = 2 Hz, 2H); NMR of 3, 3, 6, 6-d_4 -N -phenyl- 3, 6-dihydro -1, 2- oxazine ($CDCl_3$, δ): 7·25 (m, 5H), 5·95 (s, 2H).

1, 2- *d_2 -1 -Hydroxymethyl - π - allylcarboxyiron tricarbonyl lactone* **5a**. 4, 5-d_2 -N -Phenyl -3, 6- dihydro -1, 2 oxazine was treated with Fe_2 $(Co)_9$ as described for the preparation of the un-deuterated lactone **3**, and **5a** was obtained in similar yield, m.p. 112–114° (dec). NMR ($CDCl_3$, δ): 4·00 (s, 2H), 3·67 (s, 1H) 2·94 (s, 1H). The NMR spectrum at 100 MHz (acetone) revealed that the signal at 4·00 ppm is actually a doublet ($\Delta\nu \cong 1$ Hz).

3, 3 - d_2 - Hydrox - d_2 - methyl - π - allylcarboxyiron tricarbonyl lactone **6a**. This compound was prepared as described above, m.p. 112–114 (dec); NMR ($CDCl_3$, δ): 4·75 (AB q, J = 8 Hz, 2H).

1, 2 - d_2 - 1 - Anilinomethyl - π - allylcarboxyiron tricarbonyl lactam **5** *and* 1, 1 - *d_2 - anilino - d_2 - methyl - π - allylcarboxyiron tricarbonyl lactam* **6**. The lactams **5** and **6** were prepared from 4, 5 -d_2 - N - phenyl - 3, 6 - dihydro - 1, 2 - oxazine and 3, 3, 6, 6- d_4 - N - phenyl - 3, 6- dihydro - 1, 2 - oxazine respectively. The mode of preparation was identical to that which is described for **4a** (method A). NMR (Figs 2 and 3).

4 - Anilinobutan - 1 - ol **9** *and N - phenyl tetramethylene carbamate* **10**. A soln of **8** (500 mg, 3·06 mmoles) in dry benzene (12·5 ml) was stirred with $Fe_2(CO)_9$ (2·3 g, 6·12 mmoles) under N_2 at 44°. The mixture rapidly turned red and after 45 min the solids were filtered (under N_2), the filtrate evaporated and the residue chromatographed on basic alumina (III). Elution with 50% CH_2Cl_2 -hexane resulted in an oil which solidified immediately. Crystallization from hexane gave **10**, 240 mg (41%), m.p. 83–84°. (Found: C, 69·20; H, 6·66; N, 6·40; $C_{11}H_{13}NO_2$ requires: C, 69·20; H, 6·80; N, 7·32%); $\nu_{max}^{CHCl_3}$; 1500, 1600 (Ph), 1700 cm^{-1} (C=O); NMR ($CDCl_3$, δ): 7·32 (m, 8H), 4·28 (t, 2H), 3·70 (t, 2H), 1·90 (m, 4H). 4-Anilino - butan - 1-ol **9** was eluted with CH_2Cl_2 as a red oil, 76 mg (7·6%), $\nu_{max}^{CHCl_3}$; 1500, 1600 (Ph), 3350 (NH), 3550 (OH free) cm^{-1}, oxalate, m.p. 124–125° (lit. 124–125·).

Reaction in presence of water. Compound **8** (1·3 g, 8 mmoles) was vigorously stirred with $Fe_2(CO)_9$ (5·85 g, 16 mmoles) and H_2O (144 mg, 8 mmoles) in benzene (50 ml) at 45° under N_2. The evolved CO_2 was trapped by sodalime (412 mg; CO_2 calcd on the basis of water, 352 mg). After the mixture was worked up as described above, we obtained **10**, 492 mg (32%) and **9**, 453 mg (45%).

cis - 4 - Methylamino - 2 - buten - 1 - ol **11**. *cis* - 4 - Chloro - 2 -buten - 1 -ol (2g) was added to a soln of methylamine (6 g) in dry ether (20 ml) at 0°. The mixture was kept at 3° overnight. The two layers were separated by decantation, and the upper ethereal layer was dried over K_2CO_3. Removal of the ether gave the amine **11**, a bright yellow oil, 1·55 g (78%) $\nu_{max}^{CHCl_3}$; 3600 (OH free), 3360 (intramolecular OH bonded) and 1625 cm^{-1} (C=C), NMR ($CDCl_3$, δ): 5·75 (m, 2H), 4·10 (d, J = 4·5 Hz, 2H), 3·65 (s, 2H) 3·20 (d, J = 4·5 Hz, 2H), 2·4 (s, 3H).

A crystalline double adduct of the amine with phenylisocyanate was prepared and crystallized from EtOH m.p. 132–132·5°. (Found: C, 67·36; H, 6·24; N, 12·29; $C_{19}H_{21}N_3O_3$ requires: C, 67·20; H, 6·19; N, 12·39%).

2 - Methyl - 1 hydroxymethyl - π - allylcarboxyiron tri - carbonyl (actone **17**. To a solution of 16 (3g; 17 mmoles) in dry benzene (100 ml) was added $Fe_2(CO)_9$ (12·3 g, 34 mmoles) and the mixture was kept at 46° under N_2 with vigorous stirring. After 1 h the dark mixture was filtered, the filtrate acidified with 200 ml 5% HCl, washed with water and dried over $MgSO_4$. Removal of the benzene left a semi-solid residue which was chromatographed on neutral alumina (III), and the lactone **17** was eluted with benzene-CH_2Cl_2 (1 : 1) as a viscous oil (309 mg), homogeneous by TLC, $\nu_{max}^{CHCl_3}$; 1660 cm^{-1} (C=O); ν_{max}^{hexane}; 2070, 2038, 2020 cm^{-1} (C≡O), NMR ($CDCl_3$, δ): 4·66 (m, 1H), 3·99 (m, 2H), 3·54 (d,J = 1·5 Hz, 1H), 2·84 (d, J = 1·5 Hz, 1H).

1 - Methyl - 1 - anilinomethyl - π - allylcarboxyiron tricarbonyl lactam **18**. Aniline (0·2 ml) was added to a stirred soln of **17** (300 mg, 1·2 mmoles) in benzene (10 ml) containg 1 g basic alumina. After 15 h, the mixture was filtered and evaporated and the residue chromatographed on basic alumina. The lactam **18** was eluted with 50% CH_2Cl_2 - hexane, 169 mg (50%), m.p. 126–127° dec, after crystallization from CH_2Cl_2 - pentane. (Found: C, 55·01; H, 4·08; $C_{15}H_{13}FeNO_4$ requires: C, 55·20; H, 4·28%). Mass spectrum *m/e* 327 (M^+). $\nu_{max}^{CHCl_3}$; 1580 (NCOFe), 1610, 1500 cm^{-1} (Ph); ν_{max}^{hexane}; 2070, 2018, 2000 cm^{-1} (C≡O), NMR ($CDCl_3$, δ): 7·15 (m, 5H, Ph), 4·85 (dd, J = 8 and 14 Hz, 1H), 3·85 (AB q, J = 14 Hz, 2H), 3·62, (dd, J = 8 and 2 Hz, 1H), 2·85 (dd, J = 14 and 2 Hz, 1H), 2·02 (s, 3H).

N-phenyl - 1 - aza - 1, 3 - pentadieneiron tricarbonyl **19** *and* **20**. A soln of **4a** (350 mg 1·12 mmoles) in MeOH (4 ml) was refluxed for 1·5 h under N_2. (The soln develops intensive red color after about 0·5 h). The mixture was filtered and evaporated and the residue was chromatographed on basic alumina (III). The product **19** was eluted with hexane as an air-sensitive red oil which crystallized when kept under N_2, m.p. 32–35°, 160 mg (62%). This compound was identical with an authentic sample[18] prepared from crotonylideneaniline[19] and $Fe_2(CO)_9$, $\nu_{max}^{CHCl_3}$; 1480 (C=N), 1500, 1600 cm^{-1} (Ph); ν_{max}^{hexane}; 2060, 2000, 1985 cm^{-1} (C≡O). NMR (C_6D_6, δ): 6·80 (m, 5H), 6·12 (d, J = 3 Hz, 1H), 4·26 (dd, J = 9 and 3 Hz, 1H), 2·25 (q, 1H), 1·08 (d, J = 6 Hz, 3H).

The d_4-lactam **6** rearranges under the above conditions to **20**, NMR (C_6D_6, δ): 6·88 (m, 5H), 4·26 (d, J = 9 Hz, 1H), 2·25 (d, J = 9 Hz, 1H).

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