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REACTION OF TRANSITION METAL CARBONYLS WITH HETEROCYCLIC SYSTEMS.

VI *. THE INTERACTION OF $Fe_2(CO)_9$ WITH *N*-BENZYLOXYPIPERIDINE AND RELATED COMPOUNDS

Y. BLUM, Y. BECKER and Y. SHVO *
Department of Chemistry, Tel-Aviv University, Tel-Aviv (Israel)
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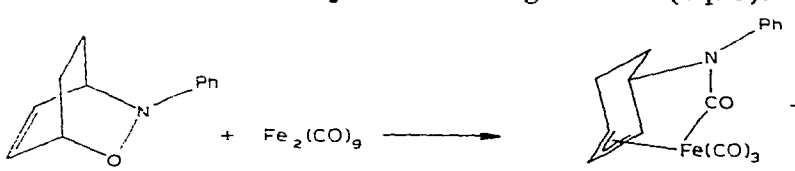
Summary

N-Benzyloxypiperidine exhibits an unexpected type of reactivity toward $Fe_2(CO)_9$. Benzaldehyde and *N*-formylpiperidine are formed, most probably in a concerted manner, as revealed by deuterium-labeling experiments. Several mechanistic details of this reaction have been elucidated. The nature of the reaction contrasts with that of *N*-propyloxy-*N*-methylaniline, which upon treatment with $Fe_2(CO)_9$ undergoes insertion of a CO group into the N—O bond to generate a carbamate.

Introduction

The reactions of the >N—O— bond have been described in several publications [1a—e]. The reactions generate a wide range of products depending on the substituents of the functional group under consideration. In systems where double bonds are incorporated in the substituents of the >N—O— functionality, the products clearly reflect the interaction of $Fe_2(CO)_9$ with both functionalities. This is best illustrated by the following reaction (eq. 1).



(1) (2) (1)

The structure of the π-allyl complex **2**, which was determined by X-ray crystallography [1d], demonstrates the concerted interaction of iron with the two functionalities of **1**. A mechanistic study revealed that **2** is an intermediate in

* For part V see ref. 1e.

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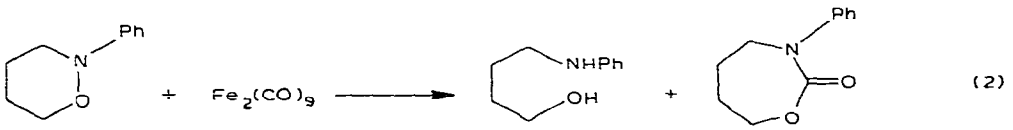
the production of the end products of reaction 1 [1d].

At one time it was thought that the reaction of the >N—O— bond with $Fe_2(CO)_9$ requires the presence of a double bond in the molecule. However, we discovered [1b] that *N*-phenyloxazine (3) reacts with the iron complex (eq. 2).

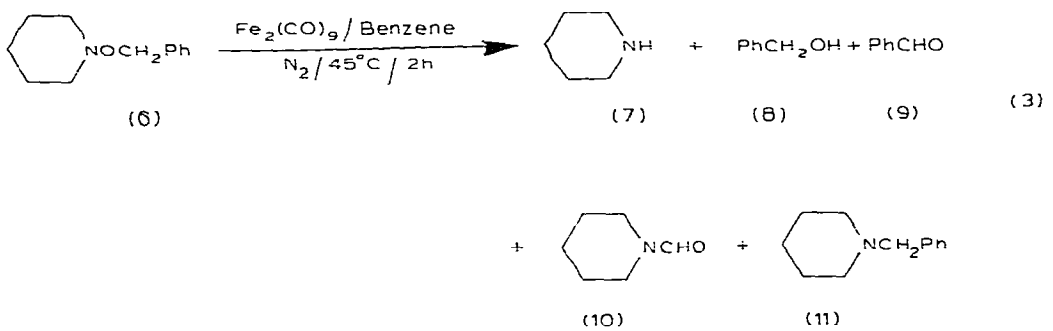


(3) (4) (5)

Although 4 is a trivial reduction product of 3, the cyclic carbamate 5 is a novel insertion product of CO into the >N—O— bond [1b]. This behavior encouraged us to examine other systems, and not only cyclic ones.

Results and discussion

The principal system investigated here is *N*-benzyloxypiperidine (6). It contains no active unsaturation; the >N—O— bond is not incorporated in a cyclic system. When 6 was treated with $Fe_2(CO)_9$ under the conditions specified in eq. 3, several products were formed.



(6) (7) (8) (9) (10) (11)

All the products were identified by GC analysis using authentic samples and then by isolation using differential solubility and chromatography.

The surprising aspects of this reaction are, on the one hand the absence of the expected carbamate, and on the other the presence of the unexpected products 9—11. None of these products were previously encountered [1]. Piperidine (7) and benzyl alcohol (8) are reduction products of types which are always formed in such reactions [1].

In order to understand the modes of formation of the various products and the reaction mechanism we monitored the kinetics of reaction 3 using GC analysis with naphthalene as internal standard. A kinetic profile of a standard run (10 mmol of *N*-benzyloxypiperidine and 20 mmol of $Fe_2(CO)_9$ in 20 ml benzene) is presented in Figure 1. Eq. 3 clearly indicates the involvement of water. Although strict precautions were taken to exclude water it was found that $Fe_2(CO)_9$ contains 0.82% of water (Karl Fisher analysis) which represents a molar ratio $H_2O/Fe_2(CO)_9$ = 1.7/1. Pyrophoric $Fe_2(CO)_9$ was produced in

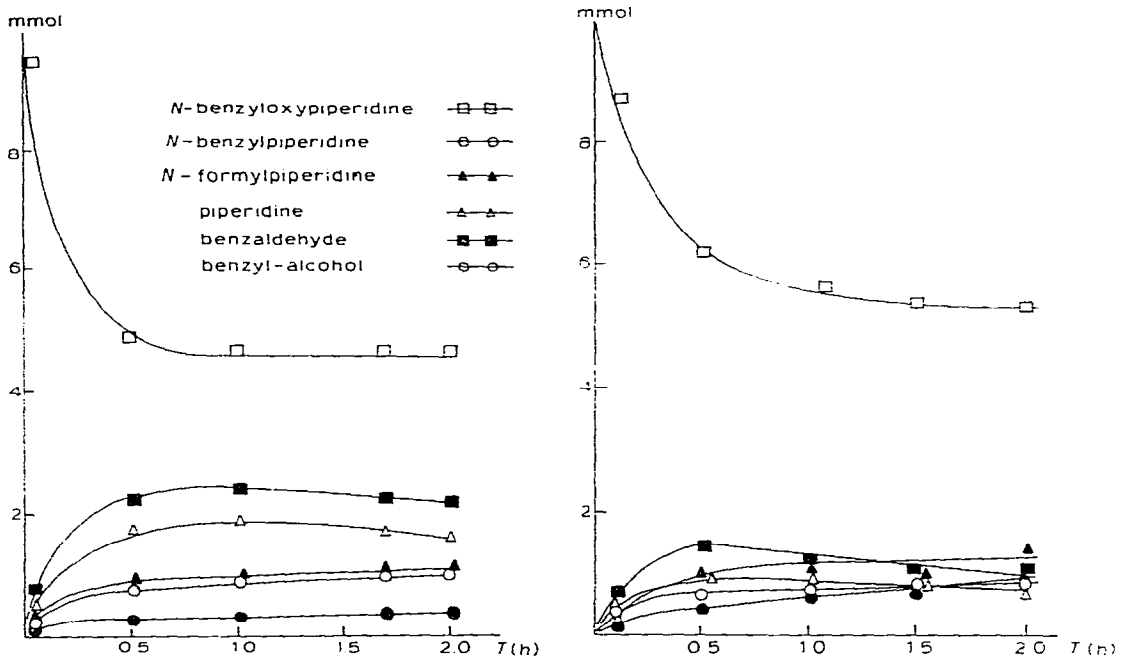


Fig. 1. The progress of the reaction between 6 and $Fe_2(CO)_9$ (quantitatively determined by GC analysis).

Fig. 2. The same reaction with a large excess of water.

attempts to remove the water (P_2O_5; 10^{-3} mm Hg). In order to examine the effect of water, reaction 3 was carried out in the presence of 50 mmoles of water and the kinetic profile is expressed in Figure 2.

Several conclusions can be drawn from the data in Figures 1 and 2.

a) The reaction ceases (~0.75 h) at 45—50% conversion of **6**, although $Fe_2(CO)_9$ is present in two fold molar excess.

b) When the concentration of **6** becomes constant (~0.75 h), those of benzaldehyde and piperidine are clearly diminishing.

c) Addition of water slightly lowers the rate of disappearance of **6**.

d) The total production of benzyl alcohol increased by a factor of ~2.5 upon addition of water, and that of benzaldehyde decreased.

For convenience the data for 0.5 and 2 hours are presented in Table 1. Analysis of the data reveals material balance of 80—83%. We have verified the presence of amines in the insoluble solids which precipitate during the reaction.

The kinetic profile data clearly indicate the occurrence of primary and secondary processes. It has to be appreciated that the presence of $Fe_2(CO)_9$, amine and water (either added or present) constitute reductive conditions [2]. Since water could not be rigorously excluded, its intervention in secondary processes was examined in the following experiments:

a) $PhCHO \rightarrow PhCH_2OH$ (4)

No reduction took place when PhCHO was subjected to the original reaction

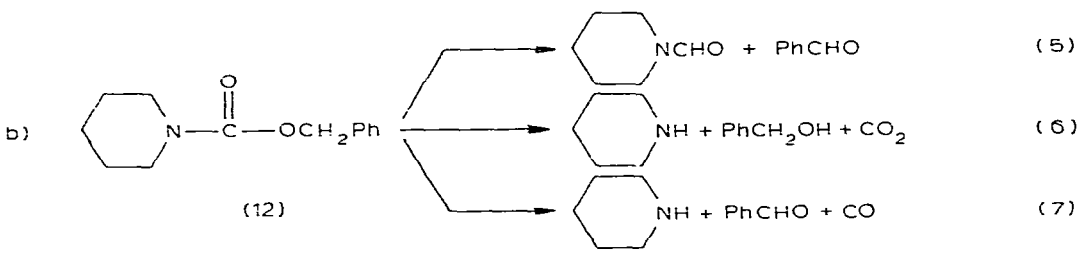
TABLE 1

PRODUCT DISTRIBUTION FROM REACTION 3 [a]

Cpd. No.	Compound	Yield (mmol)			
		Dry run		Wet run [b]	
		0.5 h	2 h	0.5 h	2 h
9	Benzaldehyde	2.30 ± 0.03	2.28 ± 0.03	1.45 ± 0.02	1.17 ± 0.02
8	Benzyl alcohol	0.35 ± 0.01	0.39 ± 0.01	0.41 ± 0.01	0.99 ± 0.01
10	*N*-Formylpiperidine	0.88 ± 0.01	0.95 ± 0.01	0.97 ± 0.01	1.42 ± 0.02
7	Piperidine [c]	1.77 ± 0.02	1.72 ± 0.02	0.89 ± 0.01	0.74 ± 0.01
11	*N*-Benzylpiperidine	0.78 ± 0.01	0.92 ± 0.01	0.58 ± 0.01	0.76 ± 0.01
6	*N*-Benzyloxypiperidine	4.88 ± 0.07	4.71 ± 0.07	6.18 ± 0.09	5.12 ± 0.07

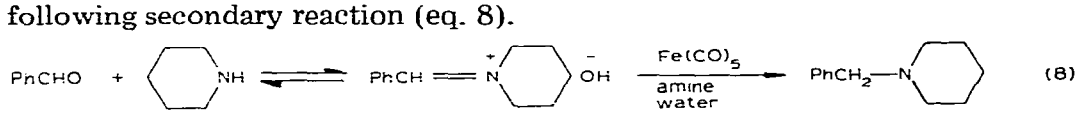
[a] The reaction was carried out with 10.0 mmol of *N*-benzylolypiperidine. All analyses were performed using GC with internal standard and appropriate sensitivity calibrations. [b] 50 mmol of water were added. [c] Since it was difficult to analyze the piperidine by GC, its quantity was calculated: **9** + **8** − **10**.

conditions using triethylamine or *N*-benzylpiperidine as base. Even in the presence of small quantities of water (10 mmol) only traces of benzyl alcohol could be detected. It is concluded that PhCHO is not a source for the total or partial production of benzyl alcohol under the conditions employed, although such reductions are known [3].



The expected carbamate (**12**) could not be detected in the product mixture. Nevertheless, it was necessary to consider its possible transient existence, expecially since its chemistry, as represented by the reaction sequence 5—7, may give rise to several products found in reaction 3. The above three reactions (5—7), were likely to occur either under the original reaction conditions, or thermally on the GC column. To that end we synthesized *O*-benzyl piperidylcarbamate and subjected it both to the original chemical reaction conditions and to the GC thermal conditions. In neither case could we detect any of the products postulated above, and the carbamate was recovered.

From the kinetic profile behavior (Figs. 1 and 2) it is evident that benzaldehyde and piperidine interacts as the reaction proceeds. This observation coupled with the observed formation of *N*-benzylpiperidine (**11**) led us to define the following secondary reaction (eq. 8).



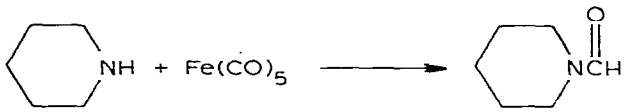
The reductive alkylation of amines with aldehyde (ketones) is an established

reaction [4]. The reduction of the imminium intermediate occurs through the intervention of $HFe(CO)_4^-$, a species generated from $Fe(CO)_5$, water and amine as base [5]. Since our reaction conditions were unusual, the above possibility was tested by bringing together piperidine, benzaldehyde and $Fe_2(CO)_9$ (molar ratio 1 : 1 : 1) in benzene under the original reaction conditions (eq. 3). *N*-benzylpiperidine was obtained (20% under such "dry" conditions and 40% when the molar ratio of piperidine : benzaldehyde : $Fe_2(CO)_9$: H_2O was 2 : 1 : 1 : 2). In our opinion, these results establish that *N*-benzylpiperidine is a secondary product, while PhCHO and piperidine are probably primary products.

Next we turned our investigation to the origin of the benzaldehyde (**9**) and formyl piperidine which were produced in reaction 3. These types of products were not encountered previously. To determine whether these are primary or secondary products, we considered two possibilities (eq. 9 and 10).

$$PhCH_2OH \rightleftharpoons PhCHO \qquad (9)$$

The possibility of a disproportionation reaction (eq. 9), induced by the complex reaction mixture, was tested. No traces of benzaldehyde were detected when benzyl alcohol was subjected to the original reaction conditions. Next, it was suspected that formyl piperidine might arise via formylation of piperidine, and Edgell [6] has demonstrated that the reaction shown in eq. 10 occurs in a hydrocarbon solvent. Although not isolated, formyl piperidine was detected by IR as

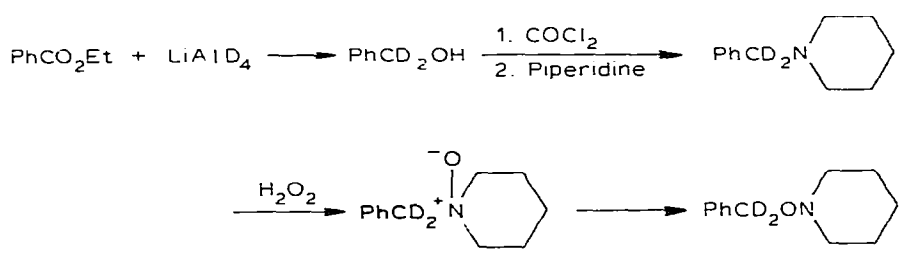


(10)

one component of the reaction mixture. We have established that formyl piperidine is not formed by treating piperidine with $Fe_2(CO)_9$ in benzene at 45°C, the original reaction conditions (eq. 3). However, formyl piperidine was formed when benzene was replaced by petroleum ether as a solvent (IR and GC analyses), in agreement with Edgell's report [6].

These two experiments demonstrate that benzaldehyde and formyl piperidine are primary products of reaction 3.

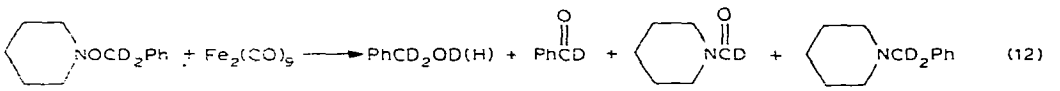
Next we directed our experiments to elucidate the mode of formation of these two compounds. It is evident that the formation of PhCHO is accompanied by the loss of a benzylic H atom from **6**. Knowledge of the fate of this H atom is important for establishing the mechanism. To this end we labeled the benzylic H atoms of **6** and prepared benzyloxypiperidine-d_2 (**13**) by the following route (eq. 11).



(11)

(13)

The isotopic purity of **13**, as determined by NMR, is >95%. Compound **13** was then treated with $Fe_2(CO)_9$, and the products, shown in eq. 12, were separated and the isotopic content of each was determined by integrating the appropriate NMR signals. Most interesting is the deuterium bound to formylpiperdine. Assuming that H_2O is still present in the reaction system, as is evident from the low deuterium content of the *N*-benzylpiperidine, the high D content of the



(13)	% D content	>95	>95	80	50

benzaldehyde (>95%) implies no equilibrium of the benzyl protons of **13**, so D (or H) is lost irreversibly. The lost D atom must be that one which appears in the formyl piperidine, which interestingly has a lower D content (80%).

Since the possibility of direct formylation of piperidine was previously excluded, we conclude that formylpiperidine and benzaldehyde are generated from the same transition state or intermediate, and we are now in a position to propose a mechanistic pathway for the reaction under consideration (Scheme 1).

The first step represents the chemical activation of $Fe_2(CO)_9$ via coordination of the reactive $Fe(CO)_4$ fragment to the N atom. Recently we described the isolation and properties of similar amine complexes [7]. That such interaction occurs in the present system was demonstrated by the appearance of three IR bands at 2055, 1965 and 1935 cm^{-1} upon treating **6** with $Fe_2(CO)_9$ in petroleum ether *. These are the frequencies which were recorded for complexes of the type $R_3N \cdot Fe(CO)_4$ [7].

Before proceeding with the mechanistic analysis two facts should be mentioned:

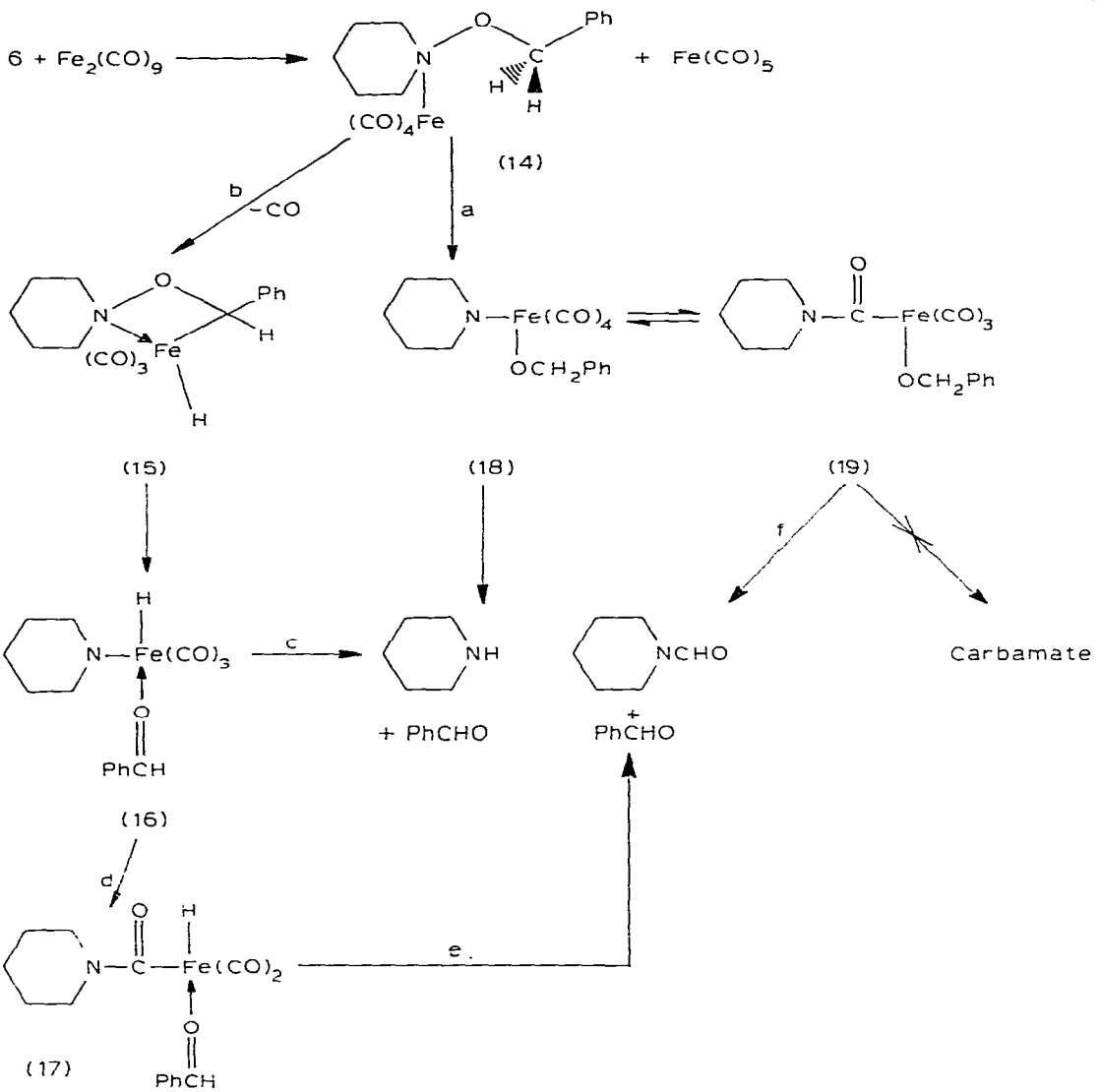
a) From Table 1 it is evident that the quantity of generated benzaldehyde (free PhCHO + benzylpiperidine) exceeds that of formylpiperidine by a factor of 2—3. It must therefore be concluded that while PhCHO and formylpiperidine are being formed simultaneously (probably in 1 : 1 ratio), PhCHO must be formed by yet another route.

b) The fact that formylpiperidine is not fully deuterated (80%) is taken as evidence for D ⇌ H exchange in an intermediate which must have an exchangeable proton, most likely in a structure such as Fe—H [8].

In Scheme 1 are outlined two principal mechanistic pathways, designated **a** and **b**, both originating from the complex **14**. They differ in the first step, i.e., oxidative addition of the metal to the >N—O— bond (route a) vs. the H—CHPhO— bond (route b). We had invoked a route a type process for all previously investigated similar systems [1d]. In these systems, viz. **1**, the oxygen atom of the >N—O— functionality was eliminated as CO_2, as reflected by the structure of the products [1b]. In the present case, however, the oxygen atom of **6** is retained in the benzaldehyde product, and in this sense the reaction patterns of **1** and **6** are different. Consequently we considered an alternative mechanism outlined in route **b** (Scheme 1). The spatial proximity and the

* There were also bands at 2020 and 2000 cm^{-1}, assigned to $Fe(CO)_5$.

SCHEME 1



enhanced reactivity of the benzylic protons may be considered as satisfactory for this oxidative addition step, which has a precedent in the literature [9]. Kinetically, the rearrangement **15** → **16** requires the cleavage of the weak >N—O— bond. Thermodynamically, the reaction may proceed due to the formation of a >C=O bond. We suggest that the products PhCHO, piperidine and formylpiperidine are formed through the partitioning of **16** between the two reaction pathways, namely **c** and **d** + **e**. These reactions involve reductive elimination of the H—Fe—N< bond (route c), and insertion of CO (route d) followed by reductive elimination (route e). Similar processes and structures have been previously invoked, and in some cases proven experimentally [10]. This scheme has two very attractive features:

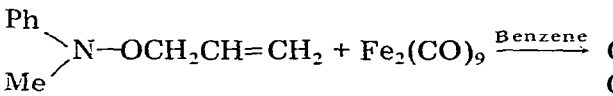
a) The partitioning of **16** between the two routes accounts for the experimentally observed products ratio: (PhCHO) > (formylpiperidine), since the former is produced by both routes.

b) Intermediates (**16** and **17**) both carry an exchangeable H atom which accounts for the lower D-content of formylpiperidine in reaction 12.

In fact route **b** and the subsequent steps adequately account for the experimental results. Quantitatively, ca. equal rate partitioning of **16** between routes **c** and **d** accounts for the observed product distribution (Table 1). However, **18** and **19** can equally well account for such a product distribution (Scheme 1). But, the mechanism of migration of the benzylic H atom to the carbamoyl carbonyl is not clear. Obviously a second oxidative addition of the metal is unreasonable, and we cannot envisage the generation of an exchangeable H.

In conclusion we favor route **b** although we have no rigorous evidence to exclude route **a**.

Next, we briefly examined two related systems, *N*-allyloxy-*N*-methylaniline [11] (**20**) and *N*-propyloxy-*N*-methylaniline [11] (**25**). The former is related to **6** inasmuch as it contains a reactive allylic H α to the oxygen atom. Its reaction with $Fe_2(CO)_9$ is represented in eq. 13.



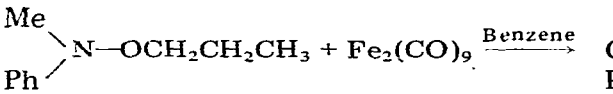
(20)

$$\xrightarrow{\text{Benzene}}$$

$CH_2{=}CHCHO$ (21, ~2%)
$CH_2{=}CHCH_2OH$ (22, 7%)
PhMeNH (23, 45%)
$PhMeNCH_2CH{=}CH_2$ (24, 10%)
+ unidentified products. (13)

In contrast with **6**, compound **20** was very reactive and completely disappeared after 20 min at 45° C. The analysis of the products was complicated by the presence of unidentifiable products. Nevertheless we could detect the presence of acrolein, both in the free and amminated form (**24**). The lack of molar equivalence between the allylic products (**21** and **22**), and **23**, is, in our opinion, due to the high chemical reactivity of the latter two compounds, which give unidentifiable by-products. The absence of *N*-formyl-*N*-methylaniline is notable, this can be rationalized in terms of modified partitioning rates when Scheme 1 is applied, i.e. either the rates via paths **b** and **f** are zero, or the rates via paths **a** and **d** are very low while **c** is operative.

Finally, the reactivity of the saturated derivative (**25**) was examined. It differs from **20** by the absence of unsaturation and from **3** in being acyclic. The results of its interaction with $Fe_2(CO)_9$ are presented in eq. 14. The reaction proceeds with 98% conversion; the products were identified by GC analysis.

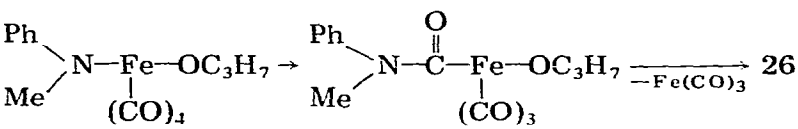


(25)

$$\xrightarrow{\text{Benzene}}$$

C_3H_7OH (36%)
PhMeNH (38%)
CH_3CH_2CHO (2%)
PhMeNPr (traces)
$PhMeNCOC_3H_7$ (26, 23%) (14)

Surprisingly, propanal is also produced by this system, though in small quantity. It is not reduced to propanol under the reaction conditions as was verified experimentally. Most striking is the production of the carbamate (**26**), and in substantial quantity, in reaction 14, in complete contrast to the two previously examined reactions. In this case we must invoke oxidative addition of the >N—O— bond to iron, similar to path **a** in scheme 1, and this would give rise to



(15)

(27) (28)

intermediate **27**. An insertion of CO followed by reductive elimination generates the carbamate **26**, as previously described [1d]. In the present case it is logical to assume that the oxidative addition of the >N—O— bond should be faster than that of the C—H bond α to the oxygen atom.

In summary we note that while any type of >N—O— bond is reactive toward $Fe_2(CO)_9$, the product pattern and distribution are highly sensitive to the nature of the substituents of the bond. With the aid of intermediates of the types **15**, **18** and **19** every product encountered in the present and past work [1] can be rationalized if it is assumed that the rates of the various steps are affected to different extents by the various substituents.

Experimental

General

Benzene (thiophene free; Fluka) was distilled from $LiAlH_4$ prior to use. All reactions were carried out under nitrogen which was purified over Cu/W at 300° C to eliminate oxygen.

Spectroscopic data were obtained with the following instruments: NMR, Jeol JMN-C-60-HL. Bruker WH-90; Mass spectra, Dupont 21-491B; IR, Perkin Elmer 177; GC, Hewlett Packard 5830 A with glass column (1.80 m) packed with SE-30 (10%) on chromosorb W.

N-Benzyloxypiperidine (6)

A solution of *N*-benzylpiperidine oxide [13] (14.0 g) in toluene (200 ml) is refluxed (4 h) with Dean-Stark azeotropic collector. The solvent was removed (vacuum), and the residue dissolved in chloroform and washed with small portions of 5% HCl to remove residual starting material. After drying and evaporation of solvent, the residue was distilled, bp. 79—81°C/0.15 mm Hg. 9.5 g (67%). Mass spec. *m/e*: 191 (M^+, $CH_{12}H_{17}NO$); NMR (CCl_4) δ: 7.32 (m, 5 H), 4.70 (s, 2 H), 2.10—360 (m, 4 H), 1.65 ppm (m, 5 H).

O-Benzyl piperidylcarbamate

Piperidine carbamoyl chloride (prepared [14] from 17.0 g piperidine and phosgene) is refluxed (2 h) with benzyl alcohol (22.0 g) in toluene. The solvent was removed (vacuum), and the residue chromatographed (silica). The carbamate was eluted with benzene-petroleum ether (1 : 1), 4.4 g, and the purity was confirmed by gas chromatography. Anal. found: C, 70.92; H, 7.66; N, 6.49.

Calcd. for $C_{13}H_{17}NO_2$: C, 71.23; H, 7.76; N, 6.39%. IR ($CHCl_3$) 1705 cm^{-1} NMR ($CDCl_3$) δ 7.33 (m, 5 H); 5.13 (s, 2 H), 3.45 (m, 4 H); 1.52 ppm (m, 6 H).

N-benzyloxypiperidine-α,α-d_2

Ethyl benzoate (0.18 mol) in dry ether (120 ml) was reduced with $LiAlD_4$ (0.12 mol). Phosgene solution (20% in toluene; 125 g) was added with stirring to the crude benzyl alcohol-α,α-d_2 obtained above (100% excess of phosgene was used), and the mixture was worked up as described in the literature [15]. The crude benzyl chloride was treated with piperidine [16]. After purification by vacuum distillation there was obtained *N*-benzylpiperidine-α,α-d_2 (13.1 g), *m/e* 177 (M^+; $C_{12}H_{15}D_2N$) with isotopic purity >95%.

The final product *N*-benzyloxypiperidine-α,α-d_2 (6.5 g) was obtained as described for the ^1H compounds, and after vacuum distillation was homogeneous by GC and had isotopic purity >95%, *m/e*: 193 (M^+; $C_{12}H_{15}D_2NO$). NMR (CCl_4) δ: 7.25 (m, 5 H); 2.36 (m, 4 H); 1.55 ppm (m, 6 H).

Reaction of N-benzyloxypiperidine and $Fe_2(CO)_9$

N-Benzyloxypiperidine (2.0 g; 11 mmol) in benzene (20 ml), naphthalene (0.42 g) as GC internal standard and $Fe_2(CO)_9$ (8 g; 22 mmol) were stirred under nitrogen for 2 h at 45°C. The reaction progress was monitored by GC using a standard solution containing known concentrations of benzaldehyde, benzyl alcohol, *N*-benzylpiperidine, formylpiperidine and naphthalene. For the 'wet' experiments, 50 mmol of water were added. The results are recorded in Figs. 1, 2 and Table 1. Similar conditions were used with benzyloxypiperidine-α,α-d_2.

Reaction of N-benzyloxypiperidine-α,α-d_2 and $Fe_2(CO)_9$

The reaction was carried out essentially as with **6**. The resulting mixture was filtered and the solids were washed with $CHCl_3$. The filtrate was concentrated to dryness and the residue dissolved in $CHCl_3$. The combined $CHCl_3$ extracts were washed with 10% aqueous HCl, until no amine was detected (GLC) in the organic phase. The aqueous phase was neutralized with 10% aqueous NaOH and the liberated oil was extracted with $CHCl_3$. GlC analysis indicated that in addition to **11** the mixture contained small amounts of **6** and **10**. The above process was repeated using 5% aqueous HCl. There was obtained a $CHCl_3$ solution of *N*-benzyloxypiperidine-α-*d*, purity 93%. Final purification was achieved by chromatography on neutral alumina column with benzene as eluent. The desired product was obtained as an oil. *m/e* 176 (M^+, $C_{13}H_{16}DN$); 175 ($M^+ - H$); 174 ($M^+ - D$); NMR ($CDCl_3$) δ: 7.1 (m, 5 H); 3.3 (s, 1 H); 2.3 (t, 4 H); 1.45 ppm (m, 6 H).

The organic phase left after the acid extraction was concentrated to dryness. The residue was sublimed under vacuum to remove naphthalene, and the naphthalene-free residue was chromatographed on a neutral alumina column. Elution with petroleum ether-benzene yielded a mixture of *N*-benzyloxypiperidine, benzaldehyde, and formylpiperidine. Further elution with petroleum ether-ethylacetate gave a mixture of formylpiperidine and benzyl alcohol. Repeated chromatography using gradient elution with chloroform-petroleum ether gave formylpiperidine-α-*d*. NMR (CCl_4) δ: 7.85 (s, 0.2 H); 3.34 (t, 4 H);

1.55 (m, 6 H); *m/e* 114 ($C_6H_{10}DNO$); 113 ($M^+ - D$); 112 ($M^+ - H(D)$). Benzylalcohol-α,α-d_2 was obtained as the major component in a mixture with formylpiperidine. NMR ($CDCl_3$) δ: 7.30 (m, 5 H), 2.4 ppm (s, 1 H).

Benzaldehyde-α-d. After extraction of the crude product mixture with 10% aqueous HCl, the organic phase was concentrated and the residue was treated with 2,4-dinitrophenylhydrazine solution. After standing for 24 h at 25°C the orange crystals were collected and washed with ethanol and petroleum ether. m.p. 243°C, *m/e* 287 (M^+, $C_{13}H_9DN_4O_4$) NMR (DMSO) δ: 11.62 (s, 1 H, exchangeable with D_2O) 8.87 (d, 1 H, J = 2 Hz) 8.38 (dd, 1 H, J = 9, 2 Hz) 8.11 (d, 1 H, J = 9 Hz) 7.64 (m, 5 H).

This spectrum is characterized by the absence of the aldehydic proton resonance at 8.71 ppm, observed in the spectrum of α-H-benzaldehyde hydrazone.

Reaction of piperidine, benzaldehyde and $Fe_2(CO)_9$

Benzaldehyde (1.08 g; 10 mmol) in benzene (20 ml) was stirred with piperidine and $Fe_2(CO)_9$ under nitrogen at room temperature for 2 h. The yield of *N*-benzylpiperidine was determined (GC) for various concentrations of the components and the results are summarized in Table 2.

Reaction of 20 with $Fe_2(CO)_9$

To a solution of **20** [11] (1.0 g; 5.8 mmol) in benzene (20 ml) containing anisole, there was added $Fe_2(CO)_9$ (2.5 g; 6.4 mmol). After stirring for 1.5 h at 45°C, the products were identified (comparison with authentic samples) and quantitatively determined by GC analysis. The results are listed in eq. 13.

Reaction of 25 with $Fe_2(CO)_9$

To a solution of *N*-propyloxy-*N*-methylaniline [17] (394 mg; 2.4 mmol) in benzene (15 ml) and anisole as external standard (93 mg) was added $Fe_2(CO)_9$ (2.04 g; 5.5 mmol). The progress of the reaction at 45°C was monitored by GC and the products (see eq. 25) were identified by comparison with authentic samples.

The carbamate **26** was isolated as follows: The crude product mixture (2 h) was filtered, washed with HCl (5%) then water. The dried solution ($MgSO_4$) was evaporated and the residue was chromatographed on neutral alumina (I) using CH_2Cl_2. When 0.8 g of **25** was used, 0.41 g of the carbamate was isolated as an oil; IR ($CHCl_3$): 1718 cm^{-1}, *m/e* (chemical ionization): 194 ($M^+ + 1$; $C_{11}H_{15}NO_2$). NMR ($CDCl_3$) δ: 7.44 (m, 5 H); 4.08 (t, J = 6.6 Hz, 2 H); 3.32 (s, 3 H); 2.58 (m, 2 H); 0.83 ppm (t, J = 6.8 Hz, 3 H).

TABLE 2

YIELD OF *N*-BENZYLPIPERIDINE FOR VARIOUS CONCENTRATIONS OF REACTION

Reactants (mmol)				% Yield of *N*-benzyl piperidine (%)
Benzaldehyde	Piperidine	$Fe_2(CO)_2$	Water	
1	1	1	—	20
1	2	1	—	28
1	2	1	2	40

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